M. Leistra

Diffusion and adsorption of the nematicide 1,3-dichloropropene in soil

Proefschrift
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Dit proefschrift met stellingen van Minze Leistra, landbouwkundig ingenieur, geboren te Ruinen op 22 juni 1942, is goedgekeurd door de promotor, dr. ir. G. H. Bolt, hoogleraar in de bodemscheikunde en de bodemnatuurkunde.

De Rector Magnificus van de Landbouwhogeschool,
J. M. Polak

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Abstract

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After soil fumigation the concentration of the nematicidal compounds *cis* and *trans* 1,3-dichloropropene at various depths in the soil was estimated by electron-capture gas-chromatography. The coefficients for the distribution of the compounds over the phases in soil under various conditions were also measured. Differential equations were derived for the events during fumigation in the field. Combinations of analytical starting solutions and numerical solutions of these equations were used. With the computation models the dose patterns in soil under various conditions could be calculated. Of the weather related factors, soil moisture had the greatest influence on efficiency of fumigation. Large clods in the plough layer caused a shade effect in the dose patterns and a rough soil surface also decreased effectiveness. After careful application differences in effectivity for various types of fumigator were small. Most of the undesirable side-effects that appear after the waiting period can be prevented by fumigating in the favourable soil moisture range and by tilling to plough depth. Estimates were made of the relative importance of disappearance by volatilization, leaching and decomposition.

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Stellingen

I

Bij de beoordeling of de omstandigheden geschikt zijn voor grondontsmetting met dichloorpropeen, verdient de vochttoestand van de bodem de grootste aandacht.

II

Het drastisch verhogen van de dosering, bij eenmalige toediening van een grondontsmettingsmiddel in de akkerbouw, is een inefficiënte en ongewenste methode om het resultaat van de bestrijding te verbeteren.

III

Het belangrijkste nadeel van grote kluiten in de bouwvoor bij grondontsmetting is dat schaduweffecten in de dosispatronen ontstaan.

IV

Bij het gebruik van afdekkingsmateriaal na grondontsmetting is de invloed van het gehalte aan organische stof van de grond op de dosis groter dan bij de toepassing zonder afdekking.

V

De controle op de deugdelijkheid van de uitvoering van grondontsmettingen dient tijdens de werkzaamheden plaats te vinden en moet vooral betrekking hebben op de werking van de injecteurs.

VI

Het aantal gevallen waarin grondontsmettingsmiddelen enkele maanden na toepassing nog gewassen beschadigen, kan aanzienlijk worden gereduceerd.

VII

Het aantal veldproeven met bodempesticiden kan tot minder dan een kwart van het huidige aantal worden teruggebracht als reeds bij de aanvang van de testperiode een aantal basisgegevens bekend is en gebruik gemaakt wordt van rekenmodellen.

VIII

Bij het ontbreken van voldoende basisgegevens en controles voor representatieve situaties, is het voorbarig om aan de hand van berekeningsresultaten adviezen voor de grondontsmetting op te stellen.

J. B. Hemwall (1960) Soil Sci. 90: 157–168.

IX

Het is noodzakelijk dat bij het beleid ten aanzien van de eventuele verontreiniging van bodem en grondwater normen worden vastgesteld die worden uitgedrukt in getallen. Deze normen dienen gekoppeld te zijn aan de bestemmingen van de grond in het kader van de ruimtelijke ordening.

Memorie van toelichting. Voorontwerp van Wet inzake de bodemverontreiniging.
Bijlagen bij de Verhandelingen van de Tweede Kamer. Zitting 1970–1971. No. 11268, p. 11.

X

Het dragen van attributen gaat gepaard met een vermindering van de lichamelijke en geestelijke mobiliteit en leidt op den duur tot irreversibele verschijnselen van deze aard.

Proefschrift van M. Leistra
Wageningen, 14 april 1972

Voorwoord

Bij het gereedkomen van dit verslag wil ik graag iedereen bedanken die een bijdrage heeft geleverd tot de totstandkoming van dit werk.

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Curriculum vitae

De auteur begon, na het behalen van het einddiploma HBS-B aan het Christelijk Lyceum in Hoogeveen, in 1959 zijn studie aan de Landbouwhogeschool te Wageningen. Na de kandidaatsstudie in de bodemkunde en bemestingsleer werd de militaire dienstplicht vervuld. Tijdens het laatste deel van de studie specialiseerde hij zich in de bodemnatuurkunde en bodemscheikunde. Vanaf het afstuderen in 1968 is hij werkzaam bij het Laboratorium voor Insecticidenonderzoek in Wageningen aan onderzoekprojecten betreffende het gedrag van bestrijdingsmiddelen in de bodem.

Samenvatting

Bij de bestrijding van schadelijke nematoden in de akkerbouw is de toepassing van grondontsmettingsmiddelen een onmisbaar hulpmiddel geworden. Met betrekkelijk lage doseringen en tegen lage kosten moet onder een grote variatie aan bodem- en weersomstandigheden een voldoende effectiviteit bereikt worden. Op het ogenblik worden voornamelijk de middelen op basis van *cis* en *trans* 1,3-dichloorpropeen gebruikt. Dit verslag houdt zich enerzijds bezig met het opsporen van de belangrijkste oorzaken van het mislukken van grondontsmettingen. Anderzijds wordt aandacht besteed aan mogelijkheden om ongewenste neveneffecten ten aanzien van de gewassen te voorkomen en ook aan verdere onderzoekbehoeften met betrekking tot de consequenties voor het milieu.

Bij een aantal veldproeven is het gedrag van *cis* en *trans* 1,3-dichloorpropeen in de bodem gevolgd. Grondmonsters, genomen van verschillende diepten en op enkele tijdstippen na het uitvoeren van de ontsmettingen, werden geëxtraheerd, waarna de concentraties werden bepaald met electron-capture gaschromatografie. Ook werden een aantal bodemfysische karakteristieken bepaald die voor het verloop van de concentratie met de tijd belangrijk zijn, zoals volumegewicht, organische stof gehalte en vochtgehalte.

Voor de kwantitatieve bestudering van het gedrag van de isomeren van 1,3-dichloorpropeen in de bodem was een aantal basisgegevens nodig. Omdat informatie betreffende de verdeling over de bodemfasen onder de verschillende omstandigheden ontbrak, werden wat dit betreft metingen verricht. Allereerst werden de coëfficiënten voor de verdeling over water en lucht gemeten. Bij adsorptiemetingen met drie gronden werd een ruwweg evenredig verband tussen de mate van adsorptie en het organische stof gehalte gevonden. Ook het effect van de temperatuur op de verdelingscoëfficiënten werd nagegaan. Een literatuurstudie betreffende de coëfficiënt voor damp- en gas-diffusie in gronden leverde voor grondmonsters in diverse toestanden schattingstrajecten op. Van de afbraaksnelheid in gronden bleek nog weinig bekend te zijn. Uit literatuurgegevens betreffende het verband tussen concentratie-tijd produkt en dodingspercentage voor parasitaire nematoden kon het belangrijkste dosistraject worden afgeleid.

Voor de beschrijving van het transport van *cis* en *trans* 1,3-dichloorpropeen door diffusie in de bodem werden differentiaalvergelijkingen afgeleid voor een- en tweedimensionale systemen. Daarbij werd rekening gehouden met de veranderingen in de waarden van de diffusie- en adsorptiekarakteristieken met plaats en tijd. Voor een periode van enkele uren na de ontsmetting konden analytische beginoplossingen

worden gebruikt, en wel de types die betrekking hebben op momentane bronnen van het grondontsmettingsmiddel. Voor het overgrote deel van de ontsmettingsperiode werden numerieke oplossingen gebruikt. Differentie-vergelijkingen van het expliciete type bleken hier het meest geschikt. Diverse vormen werden afgeleid om de concentraties te kunnen berekenen in rasterpunten gelegen in homogene lagen en in de nabijheid van overgangen tussen lagen. De computerberekeningen werden uitgevoerd aan de hand van FORTRAN programma's, die flexibel zijn ten aanzien van de te bestuderen situatie en diverse aanbouwmogelijkheden bezitten.

De berekeningen werden voor verschillende doeleinden gebruikt. Mede aan de hand van de concentratiemetingen werden de dosispatronen bij de bestudeerde grondontsmettingen berekend. Uitgaande van deze bestudeerde gevallen en met gebruik van de basisgegevens werd het afzonderlijke effect van factoren als vochtgehalte, temperatuur en organische stof gehalte nagegaan. Een andere toepassing van de rekenmodellen betrof de oriëntatie over de invloed en de ernst van verschijnselen als de aanwezigheid van kluiten in de bouwvoor, van een ruw bodemoppervlak en van natte omstandigheden tijdens de ontsmetting.

Het belang van de bodemtemperatuur is in het verleden overschat. Wat betreft de factoren die met het weer samenhangen is het vochtgehalte van de bodem verreweg de belangrijkste. Het is opvallend hoeveel moeilijkheden, zowel ten aanzien van de effectiviteit als van de ongewenste neven-effecten, kunnen worden voorkomen door bij vochtgehaltes in het gunstige traject te ontsmetten. Wat betreft de structuurtoestand is er ook een optimaal traject met aan de ene kant losse grond (bv. door frezen) met een te hoge diffusiesnelheid en aan de andere kant grond met grote kluiten die duidelijke schaduweffecten in de dosispatronen veroorzaken. Zijn er na de toepassing van het grondontsmettingsmiddel oneffenheden als kluiten en scheuren aan het bodemoppervlak dan kan de doding van de parasitaire nematoden tientallen procenten van de totale populatie lager liggen dan bij een goede afwerking het geval zou zijn geweest. Bij de in de praktijk gebruikte grondontsmettingsmachines werden geen duidelijke inherente oorzaken voor verschillen in effectiviteit gevonden. Onbevredigende resultaten met een aantal typen machines in de afgelopen jaren zijn vermoedelijk terug te voeren op factoren als onjuiste injectiediepte, verstopping van de sproeiers en slechte afwerking van het bodemoppervlak.

Ongewenste neveneffecten na de wachttijd kunnen grotendeels worden voorkomen o.a. door de doseringen op het huidige lage niveau te houden, door te stoppen met het ontsmetten onder nogal natte omstandigheden en door het uitvoeren van bewerkingen als het ploegen na de ontsmettingsperiode. Er zijn echter nog een aantal belangrijke vraagstukken, waarbij vooral de snelheid van de afbraak in bodem en lucht, en de aard en eigenschappen van de afbraakprodukten op korte termijn grote aandacht verdienen.

Contents

List of symbols

F_g = flux, μg (compound) · cm^{-2} (gas phase) · s^{-1}
F_p = flux, μg (compound) · cm^{-2} (soil) · s^{-1}
D_a = diffusion coefficient, cm^2 (gas phase) · s^{-1}
D_p = diffusion coefficient, cm^3 (gas phase) · cm^{-1} (soil) · s^{-1}
$D_{ps_{12}}$ = weighed mean D_p, series case
$D_{pp_{12}}$ = weighed mean D_p, parallel case
D_{pn} = diffusion coefficient, non-isothermal case,
μg (compound) · atm^{-1} · cm^{-1} (soil) · s^{-1}
D_m = diffusion coefficient, cm^2 (soil) · s^{-1}
C_g = concentration, μg (compound) · cm^{-3} (gas phase)
C_w = concentration, μg (compound) · cm^{-3} (water phase)
Q = fumigant contents, μg (compound) · cm^{-3} (soil)
P = partial vapour pressure, atm
x_g = space co-ordinate, cm (gas phase)
x = space co-ordinate, cm (soil)
y = space co-ordinate, cm (soil)
x_i = injection depth
(x_i, y_i) = position injection line
t = time, s
t_e = point of time end initial period, s
ε_g = volume fraction gas phase, cm^3 (gas) · cm^{-3} (soil)
ε_w = volume fraction water phase, cm^3 (water) · cm^{-3} (soil)
A_g = effective cross-sectional area, cm^2 (gas) · cm^{-2} (soil)
β = tortuosity factor, cm (soil) · cm^{-1} (gas phase)
ν = cross-section nonuniformity factor, cm (soil) · cm^{-1} (gas phase)
k_r = decomposition rate constant, s^{-1} or day^{-1}
ρ_b = bulk density, g (dry soil) · cm^{-3} (undisturbed soil)
$K_{w/g}$ = ratio between C_w and C_g
$K_{s/g}$ = ratio between μg (compound adsorbed) per g (dry soil) and C_g
$K_{om/g}$ = ratio between μg (compound adsorbed) per g (organic matter) and C_g
Φ = fumigant capacity factor, cm^3 (gas phase) · cm^{-3} (soil)
M_p = dosage, μg (compound) · cm^{-2} (soil surface)
M_s = dosage, μg (compound) · cm^{-1} (injection line)
r = factor in difference equations, dimensionless
$B(x)$ = dose, μg (compound) · cm^{-3} (water phase) · s or ppm × day

M = molecular weight, $g \cdot mol^{-1}$
R = gas constant, $litre \cdot atm \cdot mol^{-1} \cdot K^{-1}$
T = temperature, K

1 General introduction

1.1 Short survey of problems with plant-parasitic nematodes

Problems with plant-parasitic nematodes in crops are very old. Formerly it was found that, when a crop was grown in monoculture or in close rotation, yield was considerably reduced. It is likely that nematodes were often involved. Plant-parasitic nematodes were first reported in the middle of the 18th century. In the 19th century various important plant-parasitic nematodes were discovered, including stem nematodes, leaf nematodes, root-knot nematodes, and cyst-forming nematodes. Gradually it became clear that large numbers of nematodes may seriously limit crop yield and quality. A population density may increase quickly when the host crop is grown. The number of nematodes may thus be especially high with perennial crops or with annual crops in close rotation.

Plant-parasitic nematodes differ in length from 0.25 to 3 mm and in width from 0.01 to 0.5 mm. They possess a stylet, which is usually hollow and is used for piercing and feeding on tissue of plant parts both above and in the soil. Nematodes can damage plants by mechanical injury, chemico-physiological injury, withdrawing of nutrients and increasing sensitivity to drought and low temperatures. Further nematodes can be vectors for viruses and plants are made more easily accessible for pathogenic bacteria and fungi (Mai et al., 1968). Stemerding et al. (1968) reviewed nematodes, parasitic to agricultural crops, and the severe damage they cause before effective control starts. Some examples of plant nematodes that are economically important are the stem nematode (*Ditylenchus dipsaci*), root-lesion nematodes (*Pratylenchus* species), stubby-root nematodes (*Trichodorus* species), root-knot nematodes (*Meloidogyne* species), the burrowing nematode (*Radopholus similis*), the potato cyst nematode (*Heterodera rostochiensis*), and the sugar-beet nematode (*Heterodera schachtii*).

1.2 Control of potato cyst nematode

With many crops grown intensively nematode problems are encountered. Several factors determine the method of control for a certain crop. An interesting example is the control of the potato cyst nematode (*Heterodera rostochiensis*). When a susceptible potato crop is grown on fields where the nematode density is low, a 20 to 30-fold increase in population usually results. After only a few years of continual potato crops on such fields, the population of cyst-forming nematodes increases to such an extent that poorly growing patches appear and ultimately the crop fails completely.

The oldest method of control, already practised for several centuries, is crop rotation. When no host plants are present the population of the potato cyst nematode decreases by about 35% per year. However with the quick increase and the slow decrease of the population it takes many years before density falls to the initial value.

Research on breeding for resistance to the nematode has been very successful. When a resistant potato variety is grown the decrease in nematode population is approximately 80% per year. However after some years, a pathotype of the nematode multiplies that is able to overcome the resistance. At least four pathotypes (A-D) are known at the moment and it is possible that there will be more in the future. Resistance-breaking pathotypes multiply more quickly when resistant potato varieties are grown in close rotation. Other control measures may thus delay the appearance of new pathotypes.

Another practical method of control is soil fumigation, for which mainly dichloropropene mixtures are used. The rates are: 250 litres (more than 600 g active ingredient per litre) per hectare, or 175 litres (more than 850 g per litre) per hectare. Soil fumigation should reduce the number of possibly occurring nematodes by at least 80%. With these low rates it is only successful under favourable conditions and with careful application of the fumigant.

All three control measures: crop rotation, the growing of resistant potato varieties, and soil fumigation have their drawbacks. These are greatest when only one of the methods is used. Therefore a system of integrated control was designed (Hijink, 1970). When the nematode density at a site is very low, a potato crop may be grown once in two years on condition that at least once in four years a resistant potato variety is used and that once in four years the soil is also effectively fumigated.

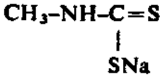
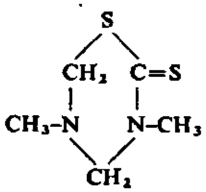
The purpose of the control methods is to prevent infestation of uninfested fields and to keep the densities of potato cyst nematode at very low levels. Many potato growers have soil samples analysed for nematodes at regular intervals. Therefore the fight against the parasite is usually at low densities, which do not affect the amount or quality of the crop yield. Whenever perceptable injury does occur, crops which act as host plant are temporarily prohibited and the soil is fumigated by split-application, twice with 250 litres of mixture (more than 600 g active ingredient per litre) per hectare. Nematode densities are determined to check the return to very low levels.

The soil fumigation that is considered in this report is mostly part of integrated control programmes. It is such an important part, however, that effectivity with low rates of fumigant and the avoidance of undesirable side-effects deserves attention.

1.3 Short review of soil fumigant application

Early in this century two soil fumigants were used to some extent: carbon disulphide and chloropicrin. Their use was limited to small areas of soil intended for growing high-value crops because large amounts of carbon disulphide were needed and chloropicrin was expensive and had to be applied with a surface cover. Chemical control with fumigants on a larger scale began when the nematicidal properties of

Table 1. Soil fumigants and fumigant precursors most frequently used at present.

Common name	Compound	Formula	Main uses
dichloropropene	1,3-dichloropropene (*cis* and *trans*)	$CH_2Cl{-}CH{=}CHCl$	nematicide
dibromochloropropane	1,2-dibromo-3-chloropropane	$CH_2Br{-}CHBr{-}CH_2Cl$	nematicide
chlorobromopropene	3-bromo-1-chloro-propene-1	$CHCl{=}CH{-}CH_2Br$	fungicide, nematicide
methyl bromide	monobromomethane	CH_3Br	fungicide, nematicide
ethylene dibromide	1,2-dibromoethane	$CH_2Br{-}CH_2Br$	nematicide
chloropicrin	trichloronitromethane	CCl_3NO_2	fungicide, nematicide
methyl isothiocyanate	methyl isothiocyanate	$CH_3{-}N{=}C{=}S$	fungicide, nematicide
metham-sodium	sodium-N-methyl-dithiocarbamate	 $CH_3{-}NH{-}\underset{\substack{\vert \\ SNa}}{C}{=}S$	fungicide, nematicide
dazomet	3,5-dimethyltetrahydro-2H-1,3,5-thiadiazine-2-thione		fungicide, nematicide

1,3-dichloropropene mixture and ethylene dibromide were discovered in the 1940's. The improvement of crop growth and the increase in yield for nematode-infested areas were so great that this soil treatment soon became popular.

Soil fumigants are nowadays widely used for the control of soilborne pathogens. Besides nematicidal and fungicidal properties, fumigants have insecticidal, phytocidal and bactericidal properties. They have rather high vapour pressures, are moderately soluble in water, and are adsorbed to a limited extent in soils. Therefore these compounds can be quickly distributed through the soil by diffusion in the gas phase. Pathogenic nematodes and fungi may thus be controlled in most of the root zone. With compounds that are not distributed so easily a good mixing is, in practice, only possible with the top layer.

The most important soil fumigants and fumigant precursors in use are given in Table 1. The first chemical group contains the volatile halogenated hydrocarbons like dichloropropene, dibromochloropropane, chlorobromopropene, and methyl bromide. Chloropicrin is a fumigant still used in horticulture, mainly against fungal diseases. Another important group contains methyl isothiocyanate and compounds which form methyl isothiocyanate as the main decomposition product after application to the soil. These precursors are metham-sodium and dazomet.

The application of soil fumigants was for a time only economically justified for high-value horticultural crops. This situation changed when prices fell for dichloropropene mixtures. In 1970, more than 30 000 hectares were fumigated in the Netherlands with this nematicide (Besemer, 1970) and the area fumigated per year is increasing. Because of a recent price drop it would also be economic to use metham-sodium for arable farming.

1.4 Some physico-chemical properties of soil fumigants

For a compound to be suitable as a soil fumigant certain properties are necessary. It must be very toxic to the parasite at low concentrations and concentration-time products. Lipophilic properties are needed to enable the nematicide to penetrate the membranes and to build up high concentrations within the nematode. There are indications that the sorption of chlorinated hydrocarbon nematicides by the nematode from the surrounding water is mainly reversible and that the sorption rates are high (Mai et al., 1968). The nematodes in the soil are nearly always surrounded by water and thus good solubility is necessary for transport from gas phase to parasite. Adsorption onto the soil organic matter must not be so strong that the compound is inactivated in the soil. High vapour pressure is another desirable property. Further the decomposition rate of the fumigant in soil has to be small compared with the diffusion rate, otherwise a good spread in the root zone is not possible.

The physico-chemical behaviour of different fumigants in soil might be similar especially within the chemical groups. It is thus interesting to compare some properties of effective soil fumigants (Table 2). The vapour pressures are higher than those

Table 2. Some important physico-chemical characteristics for the behaviour of fumigants in soil. All values for 20 °C. After Goring (1962, 1967).

Compound	Vapour pressure (mm of mercury)	Solubility in water (μg/g)	Concentration ratio		Diffusion coefficient in air[3] (cm^2/s)
			water: air[1]	org. matter: water[2]	
monobromomethane	1380	16000	4.1		0.097
1,2-dibromoethane	7.69	3370	42.7	39	0.081
cis-1,3-dichloropropene	25	2700	17.7		0.074
trans-1,3-dichloropropene	18.5	2800	24.6		0.074
1,2-dibromo-3-chloropropane	0.58	1230	164	75[4]	0.070
trichloronitromethane	20	1950	10.8		0.069
methyl isothiocyanate	21	7600	92		

1. Estimated from the solubility in water and the vapour pressure.
2. Equilibrium ratio between the amount of fumigant adsorbed per gram of organic matter and the amount of fumigant dissolved per gram of water.
3. Estimated values.
4. Determination for one soil.

for other pesticide groups. Within the group of soil fumigants, however, considerable differences are found, monobromomethane being the most volatile and 1,2-dibromo-3-chloropropane the least volatile fumigant. The solubilities in water also differ considerably. As a result of differences in vapour pressure and solubility, differences in the ratio water to air are found. Little is known about the adsorption of fumigants onto moist soils except for 1,2-dibromoethane which has been studied extensively (Wade, 1954; Call, 1957b). The values for the diffusion coefficient in air are of the same magnitude so that on account of this no great differences in the behaviour in soils are to be expected.

As with several other fumigants, there is little information on the isomers of 1,3-dichloropropene. Particularly no data in the literature are known about the distribution between the adsorbing phase and the water phase at different temperatures. More research is needed on the distribution over water and air at various temperatures in range 0–20° C. The investigations described in Section 2.1 were carried out to obtain supplementary information on the distribution of *cis* and *trans* 1,3-dichloropropene over the phases in soil.

1.5 Problems with soil fumigation in the field

In arable farming when fumigants are applied on a large scale some factors, which are not so important for fumigation in horticulture, must be considered. Cost has to be low, because there is only limited scope for investments. Therefore low rates of fumigant must be effective and inexpensive to apply. Sealing the soil surface with plastic sheeting after fumigation is still uneconomic although effective. The result of fumigation depends on the weather, which may be unfavourable in the late summer and autumn after harvesting when fields are available for fumigation. It is not easy to achieve good results. Occasionally nematode mortality percentages are insufficient and high rates of fumigant are prescribed (Spears, 1968).

The factors that have to be considered in a study on effectivity of fumigants can be divided into three groups: (1) application techniques, (2) soil composition and condition, and (3) weather conditions.

Application techniques The increase in use of soil fumigants has stimulated the development of fumigation equipment. There are often distinct differences in the results with the various types of machines, including plough injectors, subsurface-blade injectors, and shank injectors. Questions arise about possible causes for these differences. Fumigation equipment is still being developed so that it is necessary to check which constructions have the greatest chance of success. Thus the behaviour of the fumigant, after application by various techniques, should be studied quantitatively.

Soil composition and condition The organic matter content of the plough layers of the fumigated soils ranges from a few percent to about 20%. Nematode mortality percentages, obtained after field applications, indicate that soils high in organic matter content are more difficult to fumigate effectively with low rates. It is therefore interesting to know what the reason is for differences in mortality percentage and how great the differences are. A difficult situation is that in which a peat layer is immediately underneath a thin peaty-sand plough layer. A quantitative approach to this type of problem could give estimates of the extra amount of fumigant that would be needed or indicate if other requirements with respect to application technique and weather can compensate for the effect of a higher organic matter content.

With soil fumigation, questions arise about whether it is necessary to prepare the soil thoroughly. If clods and dense parts can be left between injection tracks it is important to know approximately the maximum permissable size of these heterogeneities. A related problem is how the soil surface should be finished off. Is levelling sufficient or is compressing by rolling essential? What is the quantitative effect of irregularities in the soil surface, like cracks, holes, loose injection tracks and protruding clods? To answer these questions the behaviour of the fumigant in these situations has to be studied in detail.

Weather conditions Soils are fumigated with 1,3-dichloropropene on a large scale during late summer and autumn. In this period dryer and wetter, warmer and colder periods may succeed each other. The general tendency is that temperature decreases and soil moisture content increases. Nematode mortality data from field trials show that the weather conditions have a great effect on efficiency. However, to interpret this type of data is difficult as many factors are involved. As conditions are optimum over short periods, only a small fraction of the area can be fumigated in ideal conditions. The period for soil fumigation coincides with the harvesting of important crops like potato and beet, so that only a limited amount of time is available. With crops like beet the question arises whether the soil can be fumigated effectively after harvesting which is usually late. It is unsatisfactory to have a deadline such as 15th October because the weather may vary from year to year. For optimum use of time and equipment, the suitable ranges of soil temperature and moisture content have to be defined more exactly and changes in conditions must be measured quickly. There is thus an urgent need for basic data and measuring methods that can assess the suitability of soil moisture content and temperature for fumigation.

1.6 Model approach to the behaviour of fumigants in soil with special reference to 1,3-dichloropropene

The effectivity of a soil fumigant such as 1,3-dichloropropene and its aftereffects depend on the following: fumigation equipment, fumigant rate, injection depth, layering in the soil profile, structure of the various layers, loose and denser parts in the top layer, degree of compression of the soil surface, irregularities in the soil surface, decomposition rate, organic matter content, temperature and moisture content of soil. These factors may vary considerably and occur in many different combinations. Additionally there are several soil fumigants, each with their own properties like vapour pressure, water solubility, adsorption behaviour, decomposition rate and toxicity characteristics. It would thus take much time to collect for each fumigant enough experimental evidence from separate studies to justify conclusions.

It is therefore worthwhile to try to set up models that describe quantitatively the complex event of soil fumigation. In Chapter 3 equations and solutions are given that may be suitable. In Chapter 2 basic data are discussed that are needed for the computations. An essential part of this approach is checking by measurements, which was done for fumigations with 1,3-dichloropropene in the field and is discussed in Chapter 4.

2 Basic data

2.1 Distribution of 1,3-dichloropropene over the phases in soil

For the quantitative study of the behaviour of the isomers of 1,3-dichloropropene in soil, detailed information on the distribution of these compounds over the soil phases is essential. The relative rates of the various transport phenomena are directly connected with the distribution. With volatile compounds the extent of adsorption and solution greatly influences the effective diffusion rate. The adsorption is also a very important factor in relation to the biocidal activity of an amount of fumigant present in a volume of soil. Soils that have to be fumigated exhibit a wide range of properties. Soil temperature and moisture content may show extreme variation in the period considered for this treatment. This section deals with the equilibrium distribution of 1,3-dichloropropene over the soil phases under various conditions. A satisfactory method for chemical analysis is a prerequisite and this is first described with relation to the concentrations in the gas and water phases.

2.1.1 Concentrations in gas and water phases

Concentrations were measured with an Aerograph gas-chromatograph, Model A-600-B, with an electron-capture detector with tritium source. The stainless steel column had an inner diameter of 1.5 mm and a length of 5 m. The filling consisted of 10% (w/w) Carbowax 20 M on 70 to 80 mesh Anakrom ABS. The carrier gas was pure nitrogen and the flow rate was 25 ml per min. The temperature of the injector was 170 °C, and of the column and detector 118 °C.

The recorder used was a Honeywell 1 mV with integrator. The injection liquid was *n*-hexane, 5 μl being injected at a time. The retention times for *cis* and *trans* 1,3-dichloropropene were 3.2 and 4.4 min, respectively. The standard solutions in *n*-hexane were made from *cis*-1,3-dichloropropene 99% and *trans*-1,3-dichloropropene 99% (obtained from Shell Nederland Chemie NV). The concentrations ranged from 0.1 to 2.0 μg per cm^3. Solutions of known and unknown concentrations were injected alternately. The unknown concentrations could be inferred from the calibration line.

When considering the concentration of *cis* and *trans* 1,3-dichloropropene in the gas phase it is necessary to have an idea of maximum concentrations. In Dow-laboratories, some vapour pressures were measured in the temperature range 20 to 111 °C. (Hamaker & Kerlinger, 1969; Hamaker, 1970). To estimate the vapour pressures in the temperature range 0°–20 °C the following equation may be used:

$$\log p = A - B/T$$

with p = vapour pressure in mm mercury

T = temperature in K

A and B are empirical constants.

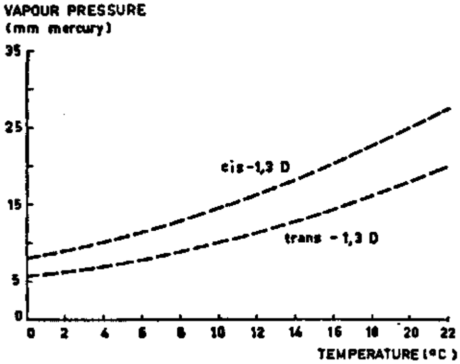


Fig. 1. Vapour pressures of *cis*-1,3-dichloropropene and *trans*-1,3-dichloropropene, estimated from measured values at higher temperatures (After Hamaker, 1970).

The results of the estimations are given in Fig. 1. The *cis* isomer seemed more volatile than the *trans* isomer. The concentrations may be calculated with the ideal gas law. The maximum concentrations of *cis*-1,3-dichloropropene ranged from 54 μg/cm³ at 0 °C to 152 μg/cm³ at 20 °C, those for *trans*-1,3-dichloropropene from 37 μg/cm³ at 0 °C to 109 μg/cm³ at 20 °C.

The concentrations in the gas phase were determined from 50 μl samples taken with a gastight 100 μl syringe. These samples were transferred to 0.5 or 1 ml of hexane in small glass tubes. From these solutions 5 μl was injected into the gas chromatograph to measure the concentration. In this way concentrations in the gas phase of 1 μg/cm³ and higher could be measured. Exploratory measurements of the saturated vapour concentration of *cis* and *trans* 1,3-dichloropropene gave results that agreed with the estimated values of the vapour pressures. When the vapour sample itself was injected, compression occurred because of the overpressure within the injector section. This resulted in losses of about 30%.

Data on the solubility in water were reported by Younson & Goring (1962):

cis-1,3-dichloropropene	2700 μg/g at 20 °C
trans-1,3-dichloropropene	2800 μg/g at 20 °C

Concentrations in water were determined by extracting 5 ml of the solution with 5 ml hexane. This solution in hexane was diluted and injected. The ratio at equilibrium of the concentration in *n*-hexane to the concentration in water was determined according to the procedure given by Voerman (1969). The ratio was 115 for *cis*-1,3-dichloropropene and 90 for *trans*-1,3-dichloropropene, so that with the *n*-hexane extraction about 1% remained in the water phase.

Distribution over water and gas phases The first distribution coefficient considered is $K_{w/g}$ which indicates the ratio at equilibrium between the concentration in the water

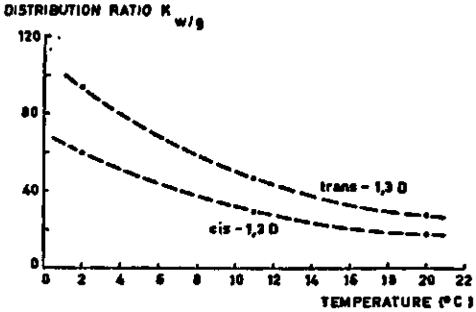


Fig. 2. Ratio $K_{w/g}$ between the concentration in the water phase and the concentration in the gas phase for *cis* and *trans* 1,3-dichloropropene at 2, 11 and 20 °C.

phase and that in the gas phase. Solutions in distilled water were made, with concentrations of approximately 100 μg/cm³. About 40 ml of these solutions were put in 120-ml flasks, which were subsequently closed by a septum wrapped in aluminum foil. During 24 h the flasks were placed in a water bath at the required temperature and shaken occasionally. After this the concentrations in the gas and water phases were determined as described.

The distribution ratios are shown in Fig. 2. These results are mean values of duplicate determinations. The standard deviation is always less than 5% of the average. In some instances this ratio was measured for a number of concentrations in the range of 100 to 1000 ppm in the water phase. The ratio $K_{w/g}$ at a certain temperature seemed independent of the concentration. This means that Henry's Law is valid: $C_w/C_g = K_{w/g}$, in which $K_{w/g}$ is Henry's constant, C_w and C_g are the concentrations in water phase and gas phase.

The value of $K_{w/g}$ was substantially higher for the *trans* isomer. This is connected with a lower vapour pressure and a slightly greater solubility in water. The estimates of the vapour pressure and the approximate values of the solubility can be used to estimate values of $K_{w/g}$ (Goring, 1967). At 20 °C, $K_{w/g} = 18$ for *cis*-1,3-dichloropropene and $K_{w/g} = 26$ for *trans*-1,3-dichloropropene. For the *cis* isomer this estimate was in good agreement with the measured value, for the *trans* isomer the estimate was slightly lower. To check the effect of salts in the soil solution, measurements were taken for solutions of 0.1 *M* calcium nitrate. There were no marked differences with the values of $K_{w/g}$ obtained for distilled water.

From the measured values of $K_{w/g}$, the relation between the solubility in water and the temperature could be estimated. The solubility could be approximated with the product of $K_{w/g}$ and the maximum concentration in the gas phase. The solubility of both isomers gradually increased with decreasing temperature. At 2 °C the solubility was about 1.27 times that at 20 °C. A similar solubility-temperature relation was reported for the soil fumigants chloropicrin and methylbromide (Stephen & Stephen, 1963).

2.1.2 Adsorption onto solid phase

The adsorbing phase As a wide variety of soils are fumigated in practice, the adsorption of 1,3-dichloropropene by different soils must be considered. The adsorption of 1,2-dibromoethane onto moist soils was studied by Wade (1954) and Call (1957b). It was found that the extent of adsorption is about proportional to the organic matter content of soil. Wade discussed the adsorption of 1,2-dibromoethane onto three soils with organic matter contents of 0.021, 0.038, and 0.24 g/g. The mean of the ratios between the amount adsorbed onto the organic matter (in μg/g) and the concentration in the gas phase (in $\mu g/cm^3$) at 20 °C was 400, while the standard deviation was 21 % of the average value. From the measurements of Call (1957b) concerned with equilibrium conditions at 15 °C for ten soils with organic matter contents in the range of 0.015 to 0.078, an average value of 460 was obtained with a standard deviation of 19 %.

The approximately linear relationship between extent of adsorption and soil organic matter content is common for pesticides that are mainly adsorbed due to van der Waals forces. Lambert et al. (1965) found such a relation for the herbicide monuron in soils containing up to 0.45 g/g organic matter. Later on, the extent of adsorption of a herbicide, an organophosphorus insecticide and a carbamate insecticide was studied in 23 soils (Lambert, 1968). The adsorption was about proportional to the organic matter content in the whole range of 0.005 to 0.40 g/g, mostly with comparatively small differences in adsorption effectivity per gram organic matter. Another example is the adsorption of the insecticide lindane onto different soils studied by Kay & Elrick (1967). Reviews of literature data on the strong correlation between the adsorption of uncharged pesticide molecules and soil organic matter content are given by Hayes (1970) and Wolcott (1970). For this type of pesticides reasonable estimates of the extent of adsorption in various soils may thus be obtained from measurements for a limited number of soils.

Adsorption measurements Adsorption was studied in three soils, humic sand, peaty sand, and peat. The organic matter contents were 0.055, 0.18, and 0.95 g per g soil, respectively. The sands were taken from plough layers, and the peat from a layer underneath the plough layer of untreated plots. These were situated in trial fields where the soil had been fumigated in the autumn of 1969 (Chapter 4).

To measure the adsorption onto soils, the 120-ml flasks were three-quarters filled with loose moist soil. After the adsorption measurements the amounts of dry soil, organic matter, and water in the flasks were determined exactly. With a small pipette, the pure liquids of *cis* and *trans* 1,3-dichloropropene were added in drops of approximately 10 mg. These amounts were weighed exactly on an analytical balance. After this the flasks were closed by the septum and put in water baths at the required temperatures. These were 2, 11 and 20 °C. The equilibrium establishment was accelerated by occasionally rotating the flasks. By sampling the gas phase at some intervals of time, the rate at which the adsorption equilibrium was established could be determined. For the soils and temperatures studied, a period of 24 h was more than sufficient. This agrees with the rates determined by Wade (1954) and Call (1957b) for the adsorption of 1,2-dibromoethane onto moist soils in flasks. Thus, the concentrations in the gas phase were measured after 24 h. The moisture contents of the humic sand, the peaty sand, and the peat were 0.17, 0.41, and 1.20 g per g, respectively.

The amount of water in the flasks, W_w, was determined by drying the flasks with the moist soil at 105 °C. After subtraction of the tare weight of the flasks, the amount of dry soil, W_s, was obtained. The amount of organic matter per flask, W_{om}, was determined with the loss-on-ignition method. The weight of the mineral parts is then: $W_{mp} = W_s - W_{om}$. For these soils the mean density of the mineral parts is $\rho_{mp} = 2.66$ g per cm^3; and for the organic matter $\rho_{om} = 1.47$ g per cm^3 (Boekel, 1961). The volumes, V, of the phases in the flasks were calculated from

$$V_{mp} = W_{mp}/\rho_{mp}, \quad V_{om} = W_{om}/\rho_{om}, \quad V_w = W_w/\rho_w,$$

and

$$V_g = 120-(V_{mp}+V_{om}+V_w).$$

The concentration in the water phase could be inferred from the concentration in the gas phase and $K_{w/g}$. The total amounts in the gas and water phases were calculated from the products of concentration and volume. The amount adsorbed was then found by subtracting the amounts in the water phase and gas phase from the amount added.

Adsorption isotherms The results of the adsorption measurements at 20 °C are shown in Fig. 3. In the concentration range used, they can be represented as linear adsorption isotherms. The same holds for the results at 11 °C and 2 °C. This is in agreement with the results of Wade (1954) and Call (1957b), who obtained linear isotherms for the adsorption of 1,2-dibromoethane onto moist soils in the relevant concentration range. From the measurements reported, the concentrations in the gas phase are, at most, about one quarter of the saturation concentration. From estimating computations and analysis of soil samples from fumigated fields, it became evident that the concentration range investigated is the most important.

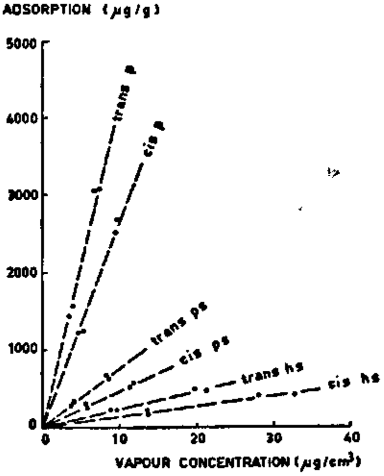


Fig. 3. Adsorption isotherms for *cis* and *trans* 1,3-dichloropropene at 20 °C. hs = humic sand, ps = peaty sand, p = peat.

Table 3. Adsorption coefficients $K_{s/g}$ for *cis* and *trans* 1,3-dichloropropene.

Soil	Temp. (°C)	$K_{s/g}$ *cis*	*trans*
Humic sand	2	38	68
	11	22	40
	20	14	24
Peaty sand	2	130	220
	11	78	130
	20	47	77
Peat	2	680	1250
	11	430	720
	20	260	410

The slope of the adsorption isotherms can be expressed in an adsorption coefficient:

$$K_{s/g} = \frac{\mu\text{g adsorbed per g of dry soil}}{\mu\text{g vapour per ml gas phase}}.$$

The values of $K_{s/g}$ are recorded in Table 3. These results are averages of four observations at different concentrations. The standard deviations were less than 5% of the average values. The adsorption of one isomer was not measurably affected by the presence of about the same amount of the other isomer.

2.1.3 Factors affecting distribution over soil phases

The effect of the soil moisture content on the total sorption (= adsorption + solution) of 1,2-dibromoethane onto soils was studied by Wade (1954). At moisture contents, corresponding with pF-values higher than about 4.2, sorption is very strong but decreases rapidly with small increases in moisture content (Fig. 4). In the range of soil moisture content from wilting point to almost saturation, the sorption increases slightly with rising moisture content. This can be attributed to the greater amount of fumigant present in the water phase. In conditions that are important for soil fumigation, the adsorption is independent of the soil moisture content. It is sufficient therefore to carry out adsorption measurements at only one soil moisture content.

It is possible to express graphically the relation between the values of $K_{s/g}$, mentioned in Table 3, and the organic matter content of the soils. From these diagrams it follows that, for the adsorption of *cis* and *trans* 1,3-dichloropropene, $K_{s/g}$ is about proportional to the organic matter content. Consequently it is useful here to define the coefficient $K_{om/g}$ for the adsorption per gram of organic matter as

$$K_{om/g} = \frac{\mu\text{g adsorbed per g of organic matter}}{\mu\text{g vapour per ml gas phase}}$$

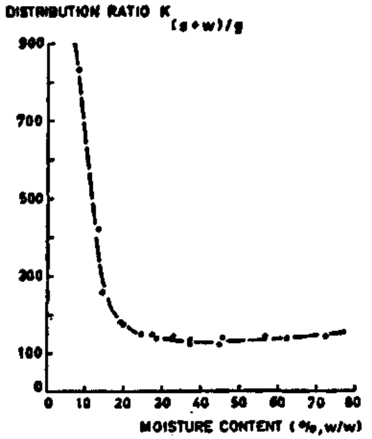


Fig. 4. Effect of moisture content of a sandy peat soil on distribution of 1,2-dibromoethane over soil plus water and air. (After Wade, 1954).

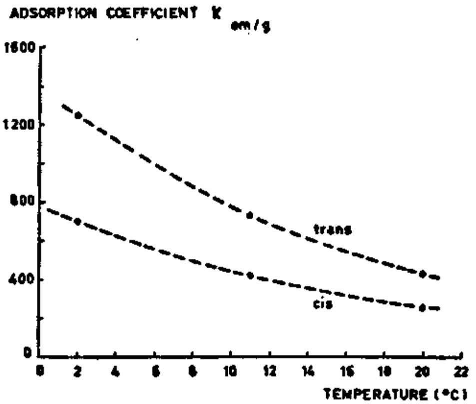


Fig. 5. Relation between $K_{om/g}$ and temperature for the adsorption of *cis* and *trans* 1,3-dichloropropene onto three soils.

The mean values of $K_{om/g}$ for the three soils were calculated. The relation between these averages and the temperature is shown in Fig. 5. The standard deviations were less than 15% of these average values. It follows that temperature had a great influence on the ratio for the distribution between the organic matter and the gas phase. At 2 °C the value of $K_{om/g}$ was about 2.8 times the value at 20 °C. For 1,2-dibromoethane the effect of temperature on sorption was studied by Wade (1954) and Call (1957b). From their results it can be calculated that the relation between $K_{om/g}$ and temperature for 1,2-dibromoethane runs parallel to the lines for the isomers of 1,3-dichloropropene.

From the coefficients $K_{om/g}$ and $K_{w/g}$, one can deduce $K_{om/w}$, indicating the distribution of the compounds over the organic matter and the water phase.

$$K_{om/w} = K_{om/g}/K_{w/g} \text{ in } \frac{\mu\text{g adsorbed per g of organic matter}}{\mu\text{g dissolved per ml water phase}}$$

Calculation of $K_{om/w}$ for *cis* and *trans* 1,3-dichloropropene gave average values of 14 and 15, respectively. From this it follows that the difference in the total sorption of the *cis* and *trans* isomer from the gas phase is mainly a result of the difference in $K_{w/g}$.

The effect of temperature on $K_{om/w}$ is not distinct, so the relation in Fig. 5 is chiefly based on the temperature effect on the water:gas distribution ratio. It was estimated in Section 2.1.1 that the water solubility of the isomers of 1,3-dichloropropene at 2 °C was about 1.27 times the solubility at 20 °C. As the ratio $K_{om/w}$ was almost constant it follows that the tendency to adsorb from the water phase varies with temperature about in the same way as the solubility in water.

The distribution coefficients discussed here can be used to calculate the percentages of *cis* and *trans* 1,3-dichloropropene in the different phases at equilibrium. This has been done for the soils studied by simulating conditions that may occur during soil fumigation in the field. For the temperature range from 2 to 20 °C, it was found that less than 1% was in the gas phase, between 10 and 20% was dissolved in the water phase, whereas between 80 and 90% was adsorbed.

2.2 Gas and vapour diffusion in soil

With the investigation of the transport of 1,3-dichloropropene in soil the question arises which soil phase is the most important for diffusion over large distances. It was shown in Section 2.1.1 that the ratio $K_{w/g}$ between the concentrations in the water and gas phases amounted to about 40 at 11 °C. On the other hand the ratio between the diffusion coefficients of 1,3-dichloropropene in the water and gas phases is about 10^{-4}. This implies that the movement over large distances in the soil is mainly a result of diffusion in the gas phase. In this respect, the diffusion in the water phase is negligible (Goring, 1967).

2.2.1 Diffusion in gas-filled pore system

Diffusion of 1,3-dichloropropene in air First the coefficient D_a for the diffusion of 1,3-dichloropropene in air is needed. The number of gas and vapour systems for which the diffusion coefficient has been measured is limited. Experimental data for 1,3-dichloropropene are not known. The value of D_a can be estimated with equations originating from the kinetic theory of gases. One or more empirical constants in these equations improve the correspondence between estimated and measured values.

Estimates of the diffusion coefficient with some of these equations were compared with measured values for more than sixty gas and vapour systems by Wilke & Lee (1955). The Hirschfelder, Bird & Spotz Method, modified by Wilke & Lee yielded

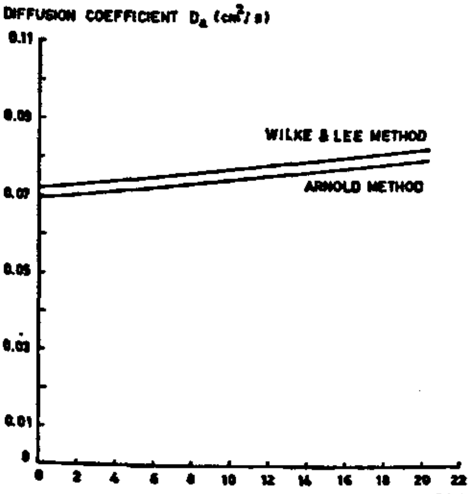


Fig. 6. Coefficients D_a for the diffusion of 1,3-dichloropropene in air calculated with Arnolds' method and with the Wilke & Lee method.

accurate results. The Arnold Method as well appeared to be suitable. The values of D_a obtained with the two methods for the 1,3-dichloropropene-air system in the range of 0-20 °C are given in Fig. 6. There is only a slight difference between the estimated values. The effect of temperature on D_a was small in the range important for soil fumigation. In the computations the averages of these estimated values were used.

Call (1957a) measured the coefficient for diffusion of the soil fumigant 1,2-dibromoethane in air. He also checked the effect of changes in the air composition. The concentrations of CO_2 that may be present in soil air, reduced the coefficient for diffusion in air by less than 1 %. The effect of water vapour also was at most 1 % of the value of the diffusion coefficient.

The gas-filled pore system If gas and vapour diffusion in soils are studied, the characteristics of the gas-filled pore system must be considered. The diffusion coefficient for a gas or vapour in this system is indicated by D_p. It is supposed that a D_p/D_a value determined for one gas or vapour is also valid for the diffusion of other volatile compounds in the soil unit, under the conditions considered (Penman, 1940).

It is useful to relate D_p/D_a and the volume fraction of gas-filled pores ε_g. The value of ε_g is determined from the bulk density of the soil, the amount and density of the soil constituents and the soil moisture content. The simplest relation is obtained for a system of cylindrical-shaped pores with the length axes in the direction of the diffusion considered: $D_p/D_a = \varepsilon_g$. Gas-filled soil pores, however, show a certain tortuosity so that the path length traversed by the molecules is greater than the effective diffusion distance. Additionally the cross-sectional area of the pores is non-uniform, resulting in a reduced effectivity for diffusion. Currie (1960) concluded for pores with a sinusoidal varying width (the cross-sectional area of the narrow parts 1/5 that of the wide parts), that the diffusion coefficient was 0.75 times that for cylindrical pores occupying the same volume fraction. An extreme situation occurs when the gas-filled pores are blocked, for example by water in the comparatively narrow places in the pore system.

Literature was reviewed to check what values of the quotient D_p/D_a could be expected for soils in various conditions. Measurements on the diffusion of gases and vapours in soils, reported in literature, were mainly in connection with aeration research. When the results were compared the differences were marked. The most probable explanation for this is that the condition of the soil samples varied considerably. Loose and dense, disturbed and undisturbed, dry and moist soils of various types were involved. In the period relevant for soil fumigation, variations of the same kind are found in field soils. It is interesting therefore to group the results of determinations on the relation between D_p/D_a and ε_g according to conditions of the soil samples.

This survey is restricted to cases in which the solution and adsorption can be neglected or in which a steady state is present. The combined effect of diffusion and distribution characteristics on fumigant transport in soil is dealt with in Chapter 3.

2.2.2 Diffusion through soil samples

Diffusion in disturbed samples of dry soils The diffusion of carbon disulphide in disturbed samples of dry soils was studied by Penman (1940) in steady state experiments. Currie (1960) obtained similar results on the diffusion of hydrogen through disturbed samples of dry soils. Penman's and Currie's results are given in Fig. 7. The lower porosities were obtained by taking mixtures of sands of different particle size. In spite of dense packing with ε_g-values in the range of 0.20, there is a good chance for diffusion.

Diffusion in disturbed samples of moist soils The steady state diffusion of 1,2-dibromoethane in disturbed moist soil samples was studied by Call (1957c). The results of diffusion measurements in sandy, loamy and peaty soils are given in Fig. 8. Call suggested the linear regression equation $D_p/D_a = 0.66\ (\varepsilon_g - 0.10)$. The ε_g range was 0.15 to 0.39. Currie (1961a) studied the diffusion of hydrogen through packings of sand and soil crumbs in moist condition. The results are also given in Fig. 8.

Fig. 9 shows results from more recent reports on measurements of diffusion coefficients D_p. Papendick & Runkles (1965) studied the diffusion of oxygen in a column with moist, silty clay-loam. Shearer et al. (1966) varied the liquid content of sand packings and measured the oxygen diffusion through the samples into a vessel originally filled with nitrogen. Grable & Siemer (1968) carried out experiments on oxygen diffusion in moist, silty clay-loam in cylinders.

Most of the measurements mentioned so far were carried out for ε_g values greater than 0.15. Gradwell (1965) achieved lower ε_g values by moderately compacting structured, moist, clay-loam. Many times in this ε_g range he found diffusion to be slight or nil (Fig. 9).

The results of the various experiments seem to be in good agreement and compared with those for disturbed samples of dry soil it follows that differences in the D_p/D_a values are small at the higher porosities near $\varepsilon_g = 0.40$. At lower porosities, however, the D_p/D_a values in the moist soils are considerably lower. This could indicate that in moist soils, the geometrical complexity of the gas-filled pore system is considerably larger in this ε_g range. For a good comparison the same soil materials should be compacted and moistened. This was done by Hannesson (1945) in a study on carbon disulphide diffusion through soil samples. From his results it follows that an increase in moisture content causes a sharper fall in diffusion rate than an equivalent compaction.

Diffusion in samples of undisturbed soil There are only a few measurements reported on diffusion in samples of undisturbed soil. Gradwell (1961) studied the diffusion of oxygen through undisturbed silt loam topsoil under pasture. The results are given in Fig. 10. Research on the diffusion of oxygen through this type of soil sample was carried out by Bakker & Hidding (1970). Their samples were taken from top layers consisting of sand, loamy sand and sandy loam.

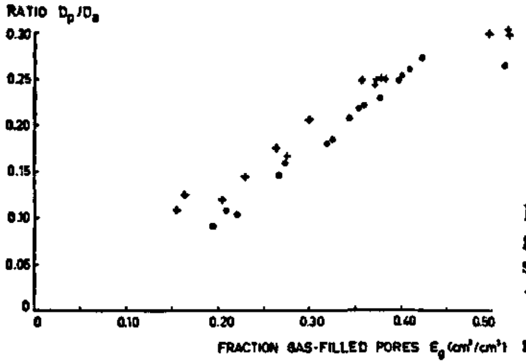


Fig. 7. Compilation of data on the diffusion of gases and vapours in disturbed samples of dry soils.

\+ Penman (1940), CS_2

● Currie (1960) for H_2 in 'sand' and 'sand mixtures'

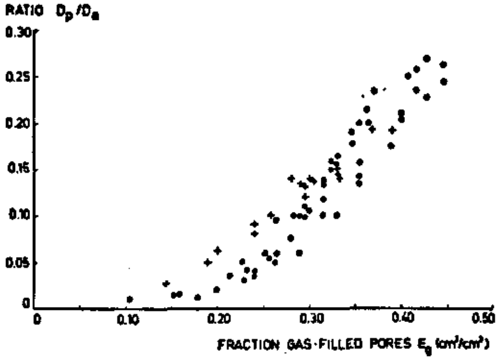


Fig. 8. Compilation of data on the diffusion of gases and vapours in disturbed samples of moist soils.

\+ Call (1957c), for 1,2-dibromoethane in various soils

● Currie (1961a) for H_2 in 'sand'

○ Currie (1961a) for H_2 in packings of soil crumbs

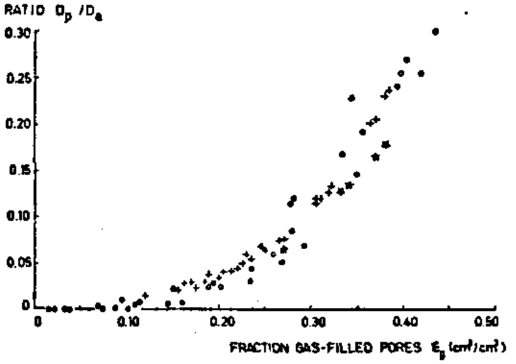


Fig. 9. Compilation of data on the diffusion of gases in disturbed samples of moist soils.

* Papendick & Runkles (1965), for O_2 in silty clay loam

● Gradwell (1965), for O_2 in clay loam

\+ Shearer et al. (1966), for O_2 in sands

○ Grable & Siemer (1968), for O_2 in silty clay loam

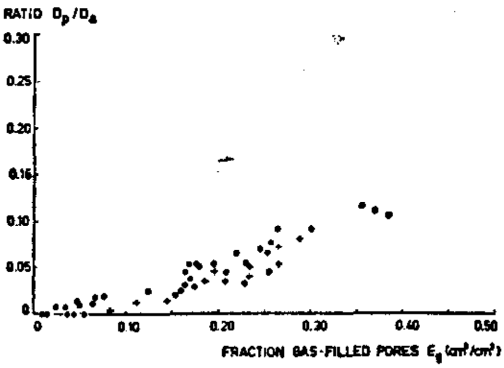


Fig. 10. Compilation of data on the diffusion of gases in samples of undisturbed soil.

● Gradwell (1961), for O_2 in silt loam

\+ Bakker & Hidding (1970), for O_2 in sand, loamy sand and sandy loam

The position of the points in the D_p/D_a against ε_g diagram corresponds with the position of the points for disturbed moist soils. In these studies, however, diffusion measurements were included for samples with a volume fraction of gas-filled pores lower than 0.10. Even in this range, diffusion was observed for a number of samples. This can probably be attributed to the effect of one or a few comparatively large pores in these soil units (Gradwell, 1961). In such a system a homogeneous distribution of gases and vapours through the soil cannot be expected.

Diffusion in structure elements It is difficult to measure coefficients for diffusion in soil structure elements. Currie (1961b, 1962, 1965) succeeded in estimating values for dry, natural, soil-crumbs. These are given in Fig. 11. In general these values lie beneath the measuring points for undisturbed samples of moist soils. It is even more difficult to estimate the diffusion coefficients for wet soil crumbs. Because the pore system in the structure elements is fine and geometrically complex, diffusion will decrease rather sharply with increasing moisture content.

Diffusion in samples of puddled soil The structure of the top layer of soil may deteriorate as a result of rainfall and tillage. Gradwell (1965) measured diffusion in some samples of compacted and puddled soil. Diffusion in puddled soil was more extensively studied by Bakker & Hidding (1970). The results are given in Fig. 12. The

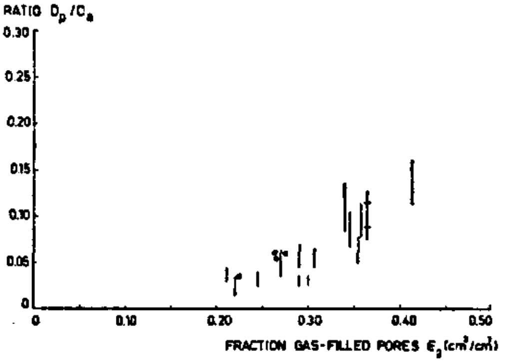


Fig. 11. Compilation of data on the diffusion of gases in structure elements.
| Currie (1961b, 1965), for H_2
● Currie (1962), for H_2

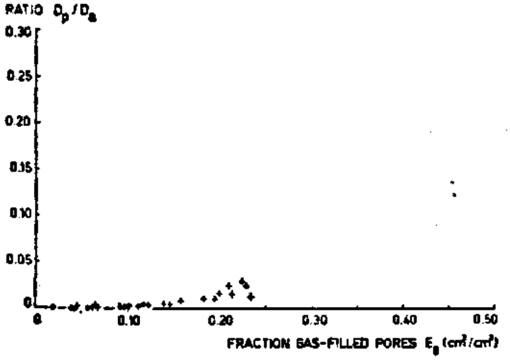


Fig. 12. Compilation of data on the diffusion of gases in samples of puddled soil.
● Gradwell (1965), for O_2 in clay loam
+ Bakker & Hidding (1970), for O_2 in sand, loamy sand, and sandy loam

values found for D_p/D_a are low and considerably lower than the values for undisturbed soil samples.

2.2.3 General remarks

The results of measurements reported in literature on the relation between D_p/D_a and ε_g were grouped according to the condition of the soil samples. The agreement between the results within the groups was better than for all the results taken together. This grouping is also useful for estimating D_p values for various parts of the soil profile such as ploughed layers, clods, plough pans and puddled top layers.

Various equations were suggested by the different authors to characterize the position of their measuring-points in the $D_p/D_a - \varepsilon_g$ diagram. Linear regression equations are not usually satisfactory. The same holds for equations of the type $D_p/D_a = \varepsilon_g^m$. Equations of the type $D_p/D_a = \gamma \cdot \varepsilon_g^\mu$ describe the position of the clusters of points rather well. The two empirical constants γ and μ, however, have different values for the various series of measurements.

To characterize the gas-filled pore system at a certain moment, the complexity parameters suggested by Currie (1960) could be used:

$$m = \log(D_p/D_a)/\log \varepsilon_g$$

and

$$k = \{\varepsilon_g/(1-\varepsilon_g)\} \cdot (D_a/D_p - 1).$$

The values of m for disturbed samples of dry soils ranged from 1.43 to 2.17 and those for k from 1.94 to 2.93. In moist soils the value of m can be 3 or more and that for k 10 or more (Currie, 1961a). High values of m and k indicate an involved geometry of the gas-filled pore system and poor diffusion possibilities.

The literature data compiled here are needed for estimations of the values of D_p to be expected in field situations. Furthermore the data can be used to predict the diffusion behaviour of 1,3-dichloropropene in various soils and soil conditions.

The lower limit of the moisture tensions, at which a favourable concentration-time relation is obtained for a great part of the soil mass, can be inferred from the relation between D_p/D_a and ε_g, and the typical moisture retention curves for a soil. Recommendations on the suitability of soil moisture conditions for fumigation can then be based upon tensiometer readings. In spite of the considerable amount of available data more research is needed on $D_p/D_a - \varepsilon_g$ relations particularly for soil samples taken from the field. There are still no experimental data for soil layers underneath a plough layer and measurements have only been carried out for a limited number of soils. For any pesticide with an important transport in the soil gas phase these data are useful.

2.3 Decomposition in soil

When the concentration-time relation for a fumigant in soil is studied it is useful to have an impression of decomposition rates. If the rate of decomposition is high, there may be a decrease in effectivity. The nature of the degradation products also has to be considered, particularly in connection with possible aftereffects of fumigation.

Decomposition reactions The decomposition of 1,3-dichloropropene in a soil was studied by Castro & Belser (1966). They found that, due to hydrolysis, one of the main products formed was 3-chloroallyl alcohol:

$CHCl=CH-CH_2Cl$ is converted to	$CHCl=CH-CH_2OH$.
1,3-dichloropropene	3-chloroallyl alcohol

The *cis* and *trans* isomerism is retained in this reaction. The nematicidal and fytocidal activity of the isomers of 3-chloroallyl alcohol is of the same magnitude as that of *trans*-1,3-dichloropropene (Moje et al., 1957). The boiling points are:

cis-3-chloroallyl alcohol	144 °C	(735 mm mercury)
trans-3-chloroallyl alcohol	154 °C	(760 mm mercury)

(Castro & Belser, 1966)

3-chloroallyl alcohol is much more soluble in water than 1,3-dichloropropene. Because of lower vapour pressure and higher water solubility the diffusion of 3-chloroallyl alcohol in the gas phase in soil is much slower than that of the original compounds. This implies that, with high decomposition rates, less 1,3-dichloropropene will be available to build up effective values of the concentration-time integral above and below the injection position. A second consequence is that, if 3-chloroallyl alcohol is slowly decomposed, there may be a long period with undesirable side-effects.

Decomposition rates It is convenient to express decomposition rate by a single figure. When information is limited to the amount decomposed in the period from zero to t, a first order reaction equation may be used:

$$dC/dt = -k_r \cdot C$$

where C is the concentration and k_r the rate constant. The initial condition is $t = 0$, $C = C_0$

Integration of the equation yields

$$k_r = -2.30 \times {}^{10}\log (C/C_0)/t$$

The rate of pesticide decomposition in soil is influenced by the nature of the pesticide, the soil type, the temperature, the moisture content, the microbial activity, the pH, and the presence of metals.

Castro & Belser (1966) determined the decomposition rate by measuring the increase in Cl^- concentration in 1 litre water with 300 g soil. Only one soil, containing organisms capable of dehalogenation, was involved and the pH was 7.5. The experiments were carried out under laboratory conditions. The decomposition rate constant k_r was approximately the same for the isomers of 1,3-dichloropropene and amounted to about 0.034 day^{-1}.

To determine the decomposition rate exactly, the amount of a decomposition product has to be measured. Sometimes, however, the magnitude of k_r can be estimated from concentrations found for the original compounds. In spring 1969, more than 10% of the 1,3-dichloropropene was still present in some fields, half a year after application. An important part probably evaporated because the soil was ploughed during winter. Here the value of k_r was considerably less than 0.01 day^{-1}. Similar results were obtained from residue analysis by Williams (1968), who measured concentrations of 1,3-dichloropropene in April, eight months after soil fumigation. With other field trials, however, the disappearance rate for 1,3-dichloropropene was too high to be explained by vapour diffusion and a low decomposition rate, in particular when some loamy soils were fumigated at high temperatures. Occasionally fytotoxicity and abnormal soil odour occurred that could not be attributed to the main ingredients of the technical dichloropropene mixtures used. Thus great differences in decomposition rate for 1,3-dichloropropene in various soil and weather conditions are indicated.

2.4 Dose and nematode mortality

Definition of dose The main object of studying the concentration-time relation for a soil fumigant under field conditions is to obtain an impression of the nematode mortality. Therefore relevant literature data were compiled. It is generally assumed that the concentration in the water phase C_w is the best measure for the nematicidal activity of the compound in moist soils because nematodes are usually surrounded by water (Goring, 1967; Mai et al., 1968).

If the concentration is constant during a period t then the dose $B(t)$ can be defined as follows: $B(t) = C_w \cdot t$. Fortunately for moderate concentrations and time intervals there is a one-to-one relationship between the mortality percentage and this dose. A decrease in concentration can be compensated by an equivalent increase in exposure time (Goring, 1957, 1967). At low concentrations, however, a detoxication mechanism may keep up with the supply of the nematicide. With short exposure periods the transport to the reactive sites may be a limiting factor. Consequently the dose resulting from these extreme situations may be less effective.

If concentration varies with time the dose can be defined as:

$$B(t) = \int_0^t C_w \, \mathrm{d}\tau .$$

The mortality percentages, obtained from experiments in which constant concentrations are maintained during period t, can be used to predict mortalities in field trials.

Table 4. Relation between concentration-time products and observed effect on nematodes from trials in water systems.

Reference	Nematode	Nematicide	Observation	Dose (ppm × day)
Mc Beth & Bergeson (1953)	*Ditylenchus dipsaci*	1,3 D	mortality 100%	220
Moje (1959)	*Tylenchulus semipenetrans*	*cis*-1,3 D	activity reduction	15
	larvae	*trans*-1,3 D	50%	35
Moje (1963)	*Tylenchulus semipenetrans*	*cis*-1,3 D	activity reduction	18
	larvae	*trans*-1,3 D	50%	40

Screen tests in water Data from the literature for trials with water systems containing nematodes and 1,3-dichloropropene are summarized in Table 4. The first trial of this type was reported by McBeth & Bergeson (1953). The concentration of 1,3-dichloropropene was calculated from the amount of dichloropropene mixture added. It is not clear from data on complete mortality percentage at what doses the percentage will be distinctly less than 100%. Two other reports (Moje, 1959, 1963) have similar experimental methods and results. The doses at which 50% mobility inhibition occurred were low. The toxicity of *cis*-1,3-dichloropropene to these nematodes was about 2.3 times that of *trans*-1,3-dichloropropene.

Trials with moist soils in sealed containers Another useful type of trial is that with nematodes, nematicides and moist soil in a sealed container. The temperature, the amount of organic matter, water and air have to be known. From the data on the distribution of 1,3-dichloropropene over the phases in soil, discussed in Section 2.1, the concentration in the water phase can be calculated. The trials of this type with the best defined concentrations were discussed by Youngson & Goring (1962, 1970). See Table 5. In other trials the only missing factor was the organic matter content of soil. Here the doses were estimated by assuming an organic matter content of 0.01 g/g soil. In some of the trials in Table 5, commercial dichloropropene mixtures were used. The contribution of the admixtures to the nematicidal action was small (Moje et al., 1957; Moje, 1959). Therefore the doses were calculated on the basis of 1,3-dichloropropene. The temperatures during the trials ranged from 20 to 25 °C.

The results represented in Tables 4 and 5 can be divided into three groups. There is a main group containing most observations. Some of the doses of this group were lower than 100 ppm × day. On account of the mortality percentages obtained in this range, percentages of about 90% can be expected at a dose of 100 ppm × day for 1,3-dichloropropene, if the contributions of both isomers to the total dose are nearly equal. This is in agreement with the 100% mortality and the non-specified high mortality obtained in the range of 110–220 ppm × day. A second group gives the results

Table 5. Dose — mortality data from trials with moist soil, nematodes and 1,3-dichloropropene in sealed containers.

Reference	Nematode	Nematicide	Observation	Dose (ppm × day)	Soil type and organic matter (g/g)
Youngson & Goring (1962)	*Meloidogyne incognita*	1,3 D	reduction gall formation		loamy sand, 0.004
			48%	28	
			97%	56	
			100%	112	
Youngson & Goring (1970)	*Heterodera schachtii*		reduction cyst formation		sandy loam 0.032
		cis-1,3 D	79%	118	
		trans-1,3 D	80%	220	
Youngson & Goring (1970)	*Pratylenchus penetrans*		activity reduction		sandy loam 0.020
		cis-1,3 D	62%	169	
		trans-1,3 D	80%	322	
Goring (1957)	*Heterodera schachtii* larvae and cysts	1,3 D	high mortality percentage	132	silt loam
Coleby et al. (1965)	*Meloidogyne javanica*		reduction gall formation		sandy loam
		1,3 D	100%	185	
Baines et al. (1966)	*Tylenchulus semipenetrans*		activity reduction		sandy loam
		1,3 D	67%	23	
			96%	34	
			99%	46	
			100%	67	
Youngson & Goring (1970)	*Meloidogyne incognita*		reduction gall formation		sandy loam
		cis-1,3 D	80%	70	
		trans-1,3 D	80%	113	

of Baines et al. (1966), which indicate that even a dose of 40 ppm × day would result in mortality percentages of 95 and more. A third group includes some of the results of Youngson & Goring (1970). Doses of about 300 ppm × day would be needed for a 90% mortality.

When the type of trial is considered, it is found that the results of the water screens belong to the main group. From the nematode species, *Tylenchulus semipenetrans* seems the most susceptible of the investigated species and then *Meloidogyne incognita.* McBeth & Bergeson (1953) and Goring (1957) found that cyst-forming nematodes were less susceptible to nematicides than certain non cyst-forming species. However the information given in their reports is too limited to estimate the relative susceptibility. From Table 5 no additional information can be obtained for *Heterodera schachtii* because results are contradictory.

Doses in field soils In field soils, the diffusion rate of the isomers of 1,3-dichloropropene has a great influence on the values of the concentration-time integral. As *trans*-1,3-dichloropropene diffuses slower than the *cis* isomer, its dose is usually higher. However the ratio between these doses is dependent on soil and weather and also varies with the distance from the injection place.

The *cis* isomer seemed more toxic to the nematodes than the *trans* isomer, but it is difficult to give a relative toxicity to the nematode species that were not studied. There is not enough information to predict relative susceptibilities of various nematode species under different conditions. At the moment only the magnitude is known of the doses needed to obtain a good nematode mortality percentage. It is preferable therefore to represent computed doses for *cis* and *trans* 1,3-dichloropropene separately, until more research has been done.

It is important to know whether the relation between mortality percentage and dose is dependent on temperature. Coleby et al. (1965) found at 15 °C a slightly lower mortality percentage for *Meloidogyne javanica* than with the same amount of dichloropropene mixture at 20 °C and higher. McBeth & Bergeson (1953) found that dichloropropene mixture was almost equally effective on *Meloidogyne* species at 7 °C and at higher temperatures. In the experiments of Youngson & Goring (1962) the toxicity of 1,3-dichloropropene to *Meloidogyne incognita* was the same at 10 °C and 18 °C.

3 Equations and solutions

3.1 Introduction

Many factors and processes are involved in the behaviour of fumigants in soil. With a compound like 1,3-dichloropropene, there is the geometry of application: the liquid may be put in the soil over a plane or a system of parallel lines. Questions arise on the rate of evaporation and on the factors which influence this rate. Diffusion in the gas phase is presumably the most important process with respect to transport over large distances in soil. However, for equilibrium to be established between the concentrations in the soil phases and the transport to the nematodes, diffusion in the water phase is important. It is also necessary to consider what happens when the majority of the gas-filled pores are blocked with water. The geometrical situation in soil is usually complex. Because of structure heterogeneities there are differences in gas-filled porosity and in the relation between diffusion coefficient and gas-filled porosity. Mainly as a result of differences in organic matter content, the extent of sorption in various parts of the soil may differ. The diffusion and sorption characteristics usually vary with space and time because of soil condition and weather-related factors. Disappearance processes are evaporation at the soil surface, diffusion and leaching into deeper layers, and chemical reactions.

The object of this study was to investigate quantitatively the problems associated with soil fumigation. Computation models were needed that would describe satisfactorily the events involved in fumigation. So far only a few studies in this field have been made. Hemwall (1959, 1960) carried out computations for hypothetical homogeneous soils and used explicit difference equations. However, the usefulness of this approach for practical soil fumigation situations is limited. At zero time, an amount of 1000 'units' was introduced at the injection position and numerical computations were carried out from this moment on. Such a discontinuous initial condition is very unfavourable for numerical computations (Crank, 1956, p. 200). Execution of diffusion computations for homogeneous soils is of limited value, especially as heterogeneities often have a decisive influence on the concentration-time relation. Frequently, difficulties are encountered with lower values of the gas-filled porosities but such conditions were not considered. Important factors like the organic matter content of soil and temperature received little or no attention. Furthermore the results of the computations were not compared with results from concentration measurements. Therefore it seemed worthwhile to study in more detail practical soil fumigation situations with computation models.

3.2 Derivation of diffusion equations

The rate of diffusion of fumigants in the gas phase in soil is considerably higher than that in the water phase. The spread throughout large volumes of soil is considered in this section. In a gas medium under isothermal conditions, the flux F_g is proportional to the concentration gradient, grad C_g (Fick's first law). Thus

$$F_g = -D_a \cdot \text{grad } C_g \tag{1}$$

In this equation D_a is called the diffusion coefficient. For diffusion in the gas-filled pore system in soils the corresponding equation is

$$F_p = -D_p \cdot \text{grad } C_g \tag{2}$$

The value of the coefficient D_p for the diffusion of the fumigant in the porous medium soil (excluding sorption) is dependent on the value of D_a and on the characteristics of the gas-filled pore system (Jackson et al., 1963). A volume element of soil of 1 cm^3 is considered, with a volume fraction of gas-filled pores ε_g, and a cross-sectional area A_g that is effective for vapour diffusion. For a system of straight pores with uniform cross-section and length axes in the direction of the diffusion considered $A_g = \varepsilon_g$ and the diffusion path length, Δx_g , is equal to the medium length Δx, so that $D_p = \varepsilon_g \cdot D_a$. When the pores with uniform cross-section show a certain tortuosity: $\Delta x/\Delta x_g < 1$.

The ratio $\Delta x/\Delta x_g$ is usually indicated by the tortuosity factor β. Then the relation between the diffusion coefficients is:

$$D_p = \beta \cdot \varepsilon_g \cdot D_a$$

Another complication is that the cross-section of the pores is non-uniform. With higher moisture contents the water may even completely block parts of the gas-filled pore system. Then the non-uniform cross-section factor $\nu = A_g/\varepsilon_g$ is less than one and $D_p = \nu \cdot \beta \cdot \varepsilon_g \cdot D_a$. Physically this relation is so complex and varies so much with soil type, structure conditions and moisture content that the most obvious procedure is to use empirical relations between D_p/D_a and ε_g. These have been discussed in Section 2.2.

The relevant conservation equation is

$$\partial Q/\partial t = -\text{div } F_p - k_r \cdot Q \tag{3}$$

The rate of change in the amount of fumigant Q per volume of soil is determined by the net result of influx and outflux and by the rate of decomposition. The latter process is described by a first order reaction equation with rate constant k_r. Substitution for F_p from the flux equation gives

$$\partial Q/\partial t = \text{div } (D_p \cdot \text{grad } C_g) - k_r \cdot Q \tag{4}$$

The distribution of an amount Q over gas phase, water phase, and adsorbing phase has been dealt with in Section 2.1. The distribution coefficient $K_{w/g}$ is independent of the concentration level. For the concentration range important for soil fumigation, linear adsorption isotherms are found so that for practical purposes a constant (i.e. concentration-independent) adsorption coefficient $K_{s/g}$ may be defined. Thus the following relation between Q and C_g is obtained:

$$Q = \varepsilon_g \cdot C_g + \varepsilon_w \cdot K_{w/g} \cdot C_g + \rho_b \cdot K_{s/g} \cdot C_g \tag{5a}$$

ε_w is the volume fraction of water-filled pores and ρ_b is the bulk density of the soil. The total fumigant capacity factor, Φ, of the system is now defined as

$$\Phi = \varepsilon_g + \varepsilon_w \cdot K_{w/g} + \rho_b \cdot K_{s/g}, \tag{6}$$

so that

$$Q = \Phi \cdot C_g \tag{5b}$$

Substitution of Equation (5b) in Equation (4) is only justified if the rate at which the equilibrium between the concentrations in the phases is established is high in comparison with the diffusion rate. Measurements of Call (1957c) on the non-stationary diffusion of 1,2-dibromoethane in soil systems support this idea.

The transport of fumigants in soil by diffusion in the gas phase is described by

$$\partial(\Phi \cdot C_g)/\partial t = \operatorname{div}(D_p \cdot \operatorname{grad} C_g) - k_r \cdot \Phi \cdot C_g \tag{7}$$

The values of the concentration in the gas phase C_g at the various positions determine the direction and rate of the diffusion, so that C_g is the most appropriate dependent variable. The coefficients Φ and D_p in this equation vary with the soil situation (and not with C_g) and are thus only position and time dependent.

Equations for plane and line sources For the large-scale application of soil fumigants plough injectors, subsurface-blade injectors and shank injectors are used. Shortly after application with the first two types of machine, the fumigant is concentrated over a plane at the injection depth. Usually the transport may then be described in a one-dimensional system in which the depth in the soil profile is the space variable x. The diffusion equation for this situation is

$$\partial(\Phi \cdot C_g)/\partial t = \partial(D_p \cdot \partial C_g/\partial x)/\partial x - k_r \cdot \Phi \cdot C_g \tag{8}$$

Immediately after the fumigant is applied with a shank injector, a set of parallel horizontal line sources of fumigant are present in the soil. The diffusion from these lines can be described in a plane perpendicular to the injection lines. Symmetry planes in relation to the diffusion patterns are the planes vertically through the injection lines and the planes vertically in the middle between these lines. These symmetry planes and the upper and lower limits of the soil profile enclose a repeating geometrical unit. The vertical axis is denoted by x (depth in the soil profile) and the horizontal axis by y (distance to the vertical plane through the injection line). Examples of this unit are shown in Fig. 20. For this two-dimensional system the following diffusion equation is obtained:

$$\partial(\Phi \cdot C_g)/\partial t = \partial(D_p \cdot \partial C_g/\partial x)/\partial x + \partial(D_p \cdot \partial C_g/\partial y)/\partial y - k_r \cdot \Phi \cdot C_g \tag{9}$$

3.3 Analytical starting solutions

The initial period Solutions of equations (8) and (9) have to be found that apply to the course of events when soil is fumigated with 1,3-dichloropropene. Usually the situation is so complex that numerical solutions are needed. However it is useful to have an analytical starting solution for the first period after fumigant application. The initial condition is discontinuous and gives rise to problems when numerical computations have to be carried out for a particular amount of fumigant. Another advantage of using an analytical starting solution is that larger space and time intervals can be taken in the numerical computations that follow. Thus much computation time is saved.

There are some alternative analytical starting solutions, with different degrees of applicability depending on conditions. For the initial condition the fumigant vaporization rate is important. This rate was determined for 1,3-dichloropropene mixture at 18 °C and the value obtained was about 0.03 mm of the liquid layer per minute. When the gas-filled porosity ε_g was 0.25, an application of 250 litres dichloropropene mixture per hectare was equivalent to a liquid film of 0.1 mm thickness. It might thus be expected that, under field conditions that are not too wet, the fumigant will vaporize quickly. This expectation is in agreement with observations on the vaporization rate of fumigants in the same volatility class as 1,3-dichloropropene (Wade, 1954; Goring, 1962). Because the vaporization rate is hardly a limiting factor with the spreading of 1,3-dichloropropene in the initial stage, solutions for instantaneous sources should be preferred.

Instantaneous plane source Immediately after application with a plough injector or a subsurface-blade injector, a fumigant is concentrated over a plane at the injection depth in soil. First the solution for an instantaneous plane source in a homogeneous soil layer is considered. Later in this section, allowance is made for a transition at the injection depth between a loose top layer and a denser layer.

After application there is an initial period with limited penetration distance. The transitions at some distance from the injection depth, the extent of the soil profile, and also the changes in conditions with time, have a negligible effect on fumigant diffusion. This implies that D_g and Φ may be considered independent of position and time so that Equation (8) becomes

$$\partial C_g/\partial t = D_m \cdot \partial^2 C_g/\partial x^2 - k_r \cdot C_g \tag{10}$$

where $D_m = D_p/\Phi$. In many cases the decomposition in a short initial period may be neglected. Equation (10) reduces then to:

$$\partial C_g/\partial t = D_m \cdot \partial^2 C_g/\partial x^2 \tag{11}$$

The initial condition is

$$t = 0 \quad x = x_i \text{ (injection depth), amount } M_p \text{ present}$$
$$x \neq x_i \qquad , C_g = 0$$

The solution of Equation (11) with these conditions is

$$C_g = [A/(t)^{\frac{1}{2}}] \cdot \mathrm{e}^{-(x-x_i)^2/(4 D_m \cdot t)} \tag{12}$$

where A is a constant. For details see Crank (1956, p. 10). This equation in only valid in the time interval $0 < t < t_e$, where t_e is the end of the initial period.

The expression for the total amount M_p in a soil column with a cross-section of one square centimeter is

$$M_p = \int_{-\infty}^{+\infty} Q \, \mathrm{d}x = \Phi \int_{-\infty}^{+\infty} C_g \, \mathrm{d}x \tag{13}$$

Substitution of Equation (12) and solving for A gives

$$A = M_p/[2\Phi(\pi D_m)^{\frac{1}{2}}] \tag{14}$$

Using this expression for A in Equation (12) gives C_g in terms of M_p:

$$C_g = \{M_p/[2\Phi \cdot (\pi \cdot D_m \cdot t)^{\frac{1}{2}}]\} \cdot \mathrm{e}^{-(x-x_i)^2/(4 D_m \cdot t)} \tag{15}$$

At time zero, the amount M_p is present at the boundary of two layers which have different properties. The variables for the layers above and below this boundary plane are denoted by the indices 1 and 2 respectively. Near this boundary at $x = x_i$ the equality $C_{g_1} = C_{g_2}$ will always be valid. From Equation (15) it follows that

$$M_{p_1}/M_{p_2} = [\Phi_1 \cdot (D_{m_1})^{\frac{1}{2}}]/[\Phi_2 \cdot (D_{m_2})^{\frac{1}{2}}] \tag{16}$$

From this equation and $M_{p_1} + M_{p_2} = M_p$, the amounts of fumigant that go upwards (M_{p_1}) and downwards (M_{p_2}) in the initial period can be calculated. The boundary plane at $x = x_i$ can be considered impermeable. Then the equation for the concentration in layer 1 at time t_e is

$$C_{g_1} = \{M_{p_1}/[\Phi_1 \cdot (\pi \cdot D_{m_1} \cdot t_e)^{\frac{1}{2}}]\} \cdot \mathrm{e}^{-(x-x_i)^2/(4 D_{m1} \cdot t_e)} \tag{17a}$$

For C_{g_2} a corresponding equation is obtained. (17b)

In soil fumigation situations an initial period of several hours can be taken. During this time a distribution is obtained that is a suitable starting point for the numerical computations.

Instantaneous line source For an instantaneous line source in a homogeneous soil layer under permanent conditions and with negligible decomposition the following special form for Equation (9) is obtained:

$$\partial C_g/\partial t = D_m \cdot \partial^2 C_g/\partial x^2 + D_m \cdot \partial^2 C_g/\partial y^2 \tag{18}$$

The initial condition is:

$t = 0$ $x = x_i$ and $y = y_i$ (injection position), amount M_s present
$x \neq x_i$ or $y \neq y_i$, $C_g = 0$

The solution for Equation (18) for the diffusion of a fumigant from an instantaneous line source into a homogeneous medium is

$$C_g = [M_s/(4\pi\,\Phi \cdot D_m \cdot t)] \cdot e^{-[(x-x_i)^2+(y-y_i)^2]/(4D_m \cdot t)} \tag{19}$$

where M_s is the amount of the compound, in µg per cm of the injection line (Crank, 1956, p. 27).

The line source, however, is situated at the transition of two layers. When the concentrations that occur during the first few hours after application were calculated, the diffusion through the transition not close to the injection line was neglected. This implies that this solution is restricted to the period in which mainly radial diffusion takes place. The variables for the layers above and below the joint plane are distinguished by the indices 1 and 2. At the injection line ($x = x_i$ and $y = y_i$) the exponential factor is equal to one and $C_{g_1} = C_{g_2}$. Thus

$$M_{s_1}/M_{s_2} = \Phi_1 \cdot D_{m_1}/(\Phi_2 \cdot D_{m_2}) \tag{20}$$

The values for M_{s_1} and M_{s_2} follow from the combination of Equation (20) and $M_{s_1}+M_{s_2} = M_s$. The concentrations at time t_e can now be calculated from

$$C_{g_1} = [M_{s_1}/(2\pi\,\Phi_1 \cdot D_{m_1} \cdot t_e)] \cdot e^{-[(x_1-x_i)^2+(y_1-y_i)^2]/(4D_{m1} \cdot t_e)} \tag{21a}$$

For layer 2 the corresponding equation with index 2 is valid (21b).

The concentrations at the joint plane were calculated by using the average D_m value. This is correct because the situation is analogous to parallel connexion in electricity theory.

Duration of the initial period with line sources The use of analytical solution (21) for the initial period is based on the presupposition that the diffusion from the line source is purely radial. The question is now, over what period this approximation might be useful. To check this, the concentrations in a humic sandy soil profile were calculated in two ways. With the first procedure the concentration pattern at $t = 6$ h was calculated by using analytical solution (21). With the second procedure the distribution after 1 h was calculated with solution (21), after which detailed numerical computations were carried out with equations (28) and (30) for the period from 1 to 6 h. The profile section important here consisted of a loose top layer and a moderately developed plough pan. The soil was somewhat dry (pF about 3) and after 6 h a fair distribution was found. In Fig. 13 the iso-concentration lines that result from the two procedures are given.

In the numerical computations, allowance is made for the diffusion from the looser top layer with a higher diffusion rate into the denser layer. This results in somewhat lower concentrations above and corresponding higher concentrations beneath the transition. However, the differences are small so that the analytical solution (21) can be used for the first hours after the application of the fumigant.

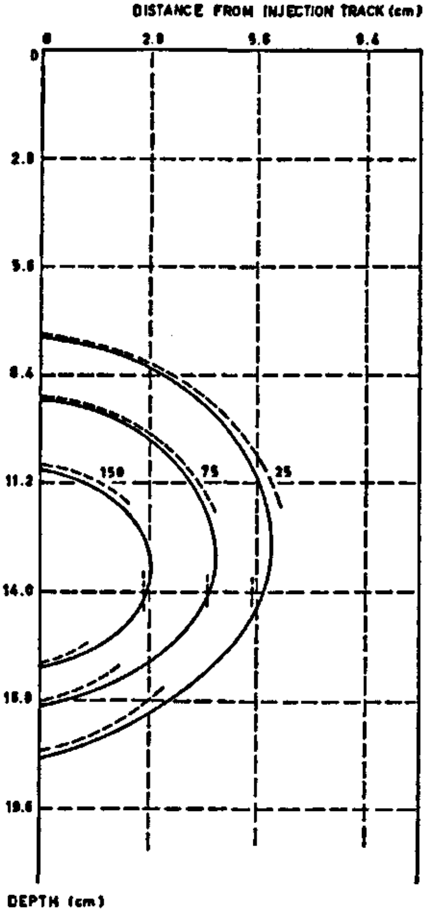


Fig. 13. Concentrations of *cis*-1,3-dichloropropene, 6 h after application with a shank injector in a humic sandy soil. Concentrations in µg per cm^3 water phase.
—— Computed *with* numerical *solutions* (28) and (30)
- - - Computed with analytical solution (21)

3.4 Numerical solution using explicit difference equations

One-dimensional system As soil fumigation is a complex process in which there are various changes with space and time, it is obvious that numerical methods are to be used. The computations are started at the time t_e at which the initial period terminates, so that the initial condition is the distribution computed with the analytical starting solution. The concentrations in the soil profile are computed for imaginary points separated by intervals of Δx cm and a time interval Δt is taken. See Fig. 14a. The boundary conditions vary according to the situation in the field. These are discussed at a later stage. There is a changeover from differential equations to equations with finite differences. Some details on this procedure were given by Crank (1956, p. 187).

For a homogeneous soil layer, Equation (10) is the starting point. $\partial C_g/\partial t$ is replaced by the forward difference and $\partial^2 C_g/\partial x^2$ by the second-order central difference approximation. The decomposition is introduced by multiplying the concentrations

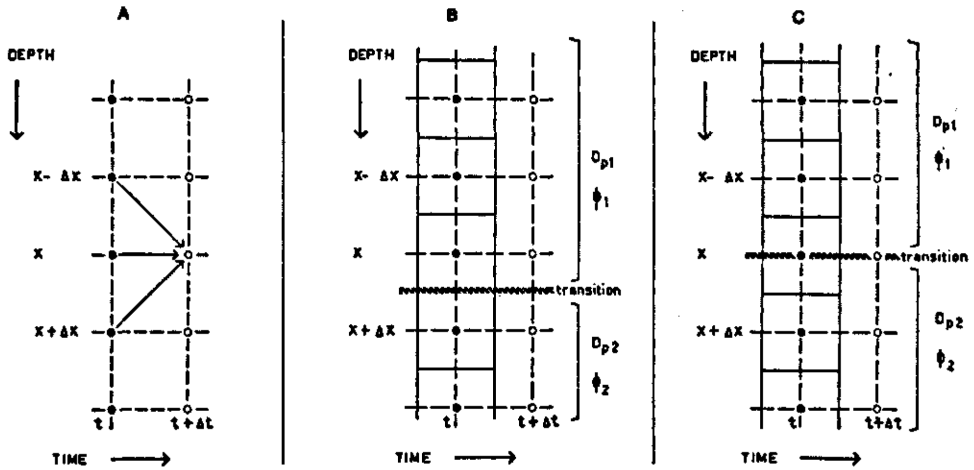


Fig. 14. Illustrations applying to the computations for the geometric one-dimensional system.
A Homogeneous soil layer. Equation (22)
B Near a transition. Equation (25)
C Near a transition. Equation (27)

with the factor $(1-k_r\cdot\Delta t)$, which is a useful approximation (Taylor's series) for the solution of the first order reaction equation with rate constant k_r. The following explicit difference equation is obtained:

$$C_g(x,\, t+\Delta t) = (1-k_r\cdot\Delta t)\,[r\cdot C_g(x-\Delta x,\, t)+(1-2r)\cdot C_g(x,\, t)+r\cdot C_g(x+\Delta x,\, t)] \tag{22}$$

where $r = D_m\cdot\Delta t/(\Delta x)^2$. For quick numerical computations large time intervals are desired. From the definition of r and from the stability condition $r \leqslant 0.5$ it follows that

$$\Delta t \leqslant 0.5\cdot(\Delta x)^2/D_m \tag{23}$$

With increasing Δx the maximum Δt allowed increases rapidly.

In heterogeneous soils, transitions are found between sections of the soil that have different properties with regard to the fumigant. This is shown in the variation of D_p and Φ with the position in the soil profile. So the model considerations (Crank, 1956, p. 204) have to be based on Equation (8). Then diffusion can be most clearly visualized by dividing the soil into imaginary geometrical sections (Franks, 1966).

Suppose that there are two adjacent layers and the sections can be arranged in such a way that the transition between the layers coincides with the transition between two sections. See Fig. 14b. One new equation is introduced now for the flux between the section at position $x+\Delta x$ and that at x:

$$\text{Flux}(x+\Delta x \rightarrow x) = -D_{ps_{12}}[C_g(x+\Delta x,\, t)-C_g(x,\, t)]/\Delta x \tag{24}$$

$D_{ps_{12}}$ is the weighed mean diffusion coefficient which can be calculated from $1/D_{ps_{12}}=$

$0.5(1/D_{p_1}+1/D_{p_2})$. This follows from the analogy with series connexion in electricity theory. The following difference equation is obtained:

$$C_g(x, t+\Delta t) = (1-k_r\Delta t)\,[(1-r_1-r_{121})\cdot C_g(x, t)+r_1\cdot C_g(x-\Delta x, t)+ \\ +r_{121}\cdot C_g(x+\Delta x, t)] \tag{25}$$

where

$$r_1 = (D_{p_1}/\Phi_1)\cdot \Delta t/(\Delta x)^2$$

and

$$r_{121} = (D_{ps_{12}}/\Phi_1)\cdot \Delta t/(\Delta x)^2$$

It is convenient to have some choice when arranging the imaginary sections. For that purpose an equation is used for the situation outlined in Fig. 14c. The finite difference approximation for the left term in Equation (8) is given by

$$\partial(\Phi\cdot C_g)/\partial t = [\Phi_{12}\cdot C_g(x, t+\Delta t)-\Phi_{12}\cdot C_g(x, t)]/\Delta t \tag{26}$$

in which Φ_{12} is the average of the values of Φ_1 and Φ_2. The difference equation that arises from this is

$$C_g(x, t+\Delta t) = (1-k_r\cdot\Delta t)\,[(1-r_{112}-r_{212})\cdot C_g(x, t)+r_{112}\cdot C_g(x-\Delta x, t)+ \\ +r_{212}\cdot C_g(x+\Delta x, t)] \tag{27}$$

where

$$r_{112} = (D_{p_1}/\Phi_{12})\cdot \Delta t/(\Delta x)^2$$

and

$$r_{212} = (D_{p_2}/\Phi_{12})\cdot \Delta t/(\Delta x)^2$$

Two-dimensional system The diffusion after shank injection can be described in a repeating geometrical unit marked out by the limits of the soil profile and the vertical symmetry planes (Section 3.2). Over this unit a imaginary square grid of points is placed. The concentrations and doses at these points are calculated. Mostly a grid interval of about 3 cm is taken. The grid is selected in such a way that the intersection of the injection line coincides with a grid point.

To form an explicit difference equation for a homogeneous layer, Equation (18) plus decomposition term is used and the result is

$$C_g(x, y, t+\Delta t) = (1-k_r\cdot\Delta t)\cdot\{(1-4r)\cdot C_g(x, y, t)+r[C_g(x-\Delta x, y, t)+ \\ +C_g(x+\Delta x, y, t)+C_g(x, y-\Delta y, t)+C_g(x, y+\Delta y, t)]\} \tag{28}$$

where $r = D_m\cdot\Delta t/(\Delta x)^2$. The stability condition for Equation (28) is $r \leq 0.25$. An illustration is given in Fig. 15A.

To compute the concentrations at the grid points near the transitions between the layers, special difference equations are derived. The indices 1 and 2 are used for the layers above and below an arbitrary transition plane. The first case considered is that in which the grid points are situated on either side of the transition. See Fig. 15B. The

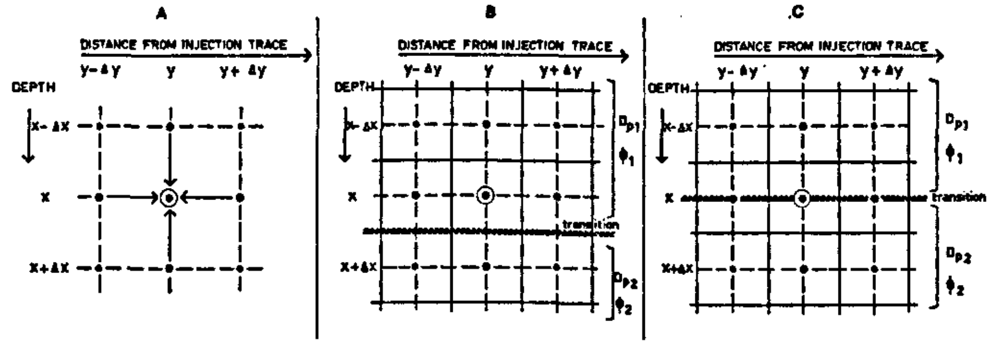


Fig. 15. Illustrations of how the computations for the geometric two-dimensional system are carried out. (A) Homogeneous layer. Equation (28). (B) Grid points at either sides of a transition. Equation (29). (C) Series of grid points through a transition. Equation (30).

difference equation derived from Equation (9) for the array of points above the transition is

$$\begin{aligned} C_g(x, y, t+\Delta t) = (1-k_r \cdot \Delta t) \cdot \{&(1-3r_1-r_{121}) \cdot C_g(x, y, t)+ \\ &+r_1[C_g(x-\Delta x, y, t)+C_g(x, y-\Delta y, t)+C_g(x, y+\Delta y, t)]+ \\ &+r_{121} \cdot C_g(x+\Delta x, y, t)\} \end{aligned} \tag{29}$$

where

$$r_1 = D_{m_1} \cdot \Delta t/(\Delta x)^2$$

and

$$r_{121} = (D_{ps_{12}}/\Phi_1) \cdot \Delta t/(\Delta x)^2$$

A similar equation is obtained for the concentrations in the array of points under the transition.

The second case considered is that in which an array of grid points coincides with a transition between two layers. See Fig. 15C. The difference equation for the concentrations in this array of points, following from Equation (9) is

$$\begin{aligned} C_g(x, y, t+\Delta t) = (1-k_r \cdot \Delta t) \cdot \{&(1-2r_{12}-r_{112}-r_{212}) \cdot C_g(x, y, t)+ \\ &+r_{12}[C_g(x, y-\Delta y, t)+C_g(x, y+\Delta y, t)]+r_{112} \cdot C_g(x-\Delta x, y, t)+ \\ &+r_{212} \cdot C_g(x+\Delta x, y, t)\} \end{aligned} \tag{30}$$

where

$$r_{12} = (D_{pp_{12}}/\Phi_{12}) \cdot \Delta t/(\Delta x)^2$$
$$r_{112} = (D_{p_1}/\Phi_{12}) \cdot \Delta t/(\Delta x)^2$$

and

$$r_{212} = (D_{p_2}/\Phi_{12}) \cdot \Delta t/(\Delta x)^2$$

From the definition of r and the stability condition it follows that the time interval Δt is restricted by the greatest D_p/Φ-value for a profile.

3.5 Check of numerical solutions

When using an explicit difference equation in a one-dimensional system the following condition has to be met: $(D_p/\Phi) \cdot \Delta t/(\Delta x)^2 \leqslant 0.5$. In view of the information required from the computations a space interval Δx of about 3 cm is usually selected. Δt is limited by Δx and by the maximum value of D_p/Φ in the profile: $\Delta t \leqslant 0.5 (\Delta x)^2/(D_p/\Phi)_{max}$. Check runs (Crank, 1956, p. 201) were made to see if the accuracy of the finite difference approximations was affected by the size of time and space intervals. Computations were carried out for a one-dimensional system with equations (22), (25) and (27). Computations with the maximum allowed time step and those with half this time step gave similar results for concentrations and doses. This is principally because an analytical starting solution was used, which provides a smooth initial condition for the numerical computations.

Runs with the combination $\Delta x/2$ and $\Delta t/4$ for a layered soil profile gave the same results as those for Δx and Δt. This implies that if the sections (Fig. 14), with the transition quantities $D_{p_{12}}$ and Φ_{12}, are varied in size in the ranges normally used, the results are hardly affected.

3.6 Alternative numerical solutions

Alternatives to solve parabolic differential equations numerically are implicit procedures, whose advantage is that longer time intervals can be taken. An implicit method was used for Equation (8), dealing with diffusion in a layered soil to which the fumigant is applied as a plane source. The distribution of the fumigant at the end of the initial period was calculated using the analytical solution (17). For computations after this short period, the Crank-Nicolson implicit method was used. The equations were obtained by adding the second-order central difference approximations at t and $t+\Delta t$, and equating to twice the forward difference approximation in the time direction for grid point (x, t) (Crank, 1956, p. 189). The result is a set of simultaneous equations of the following type:

$$\begin{aligned} &-r(xm) \cdot C_g(x-\Delta x, t+\Delta t) + [2+r(xm)+r(xp)] \cdot C_g(x, t+\Delta t) \\ &\quad -r(xp) \cdot C_g(x+\Delta x, t+\Delta t) = r(xm) \cdot C_g(x-\Delta x, t) + \\ &\quad +[2-r(xm)-r(xp)] \cdot C_g(x, t) + r(xp) \cdot C_g(x+\Delta x, t) \end{aligned} \tag{31}$$

with

$$r(xm) = [D_p(xm)/\Phi(x)] \cdot \Delta t/(\Delta x)^2$$

and

$$r(xp) = [D_p(xp)/\Phi(x)] \cdot \Delta t/(\Delta x)^2$$

In this xm refers to the interval between x and $x-\Delta x$, while xp refers to the interval from x to $x+\Delta x$. Many values are obtained for the coefficients r due to variations in D_p and Φ in the soil profile.

A computation scheme based on Gauss's elimination method was used to solve the set of simultaneous equations (Smith, 1969, p. 20). For comparison, computations for the same situation were carried out with the explicit method. The results of the implicit and the explicit methods used were in good agreement, both for the concentrations and the doses. The deviation between the results was in the range of 0 to 4% of the average values.

With the implicit method more time was needed for the preparatory calculations because many coefficients had to be evaluated. Regularly the values of the concentration-time integral had to be computed so that a very large time interval could not be taken. As a result more time was also needed for the computer calculations. For soil fumigation situations, the Crank-Nicolson method may be advantageous when concentrations have to be considered that occur a long time after the application of the fumigant. This is the case with the questions concerning the period with possible aftereffects.

3.7 Non-isothermal conditions

When studying the suitability of conditions for soil fumigation, it is occasionally necessary to consider the effect of changes in temperature with depth. The upper centimeters of soil may be considerably warmed up by radiation on sunny days. With differences in temperature there is more variation in the value of diffusion and adsorption characteristics in the soil profile. This can be accounted for by introducing more layers in the computation model. Another complication in the computations is that the concentration in the gas phase C_g is no longer a suitable dependent variable because the relation between C_g and the pressure P(atm) of the compound varies with temperature (ideal gas law). The diffusion flux is virtually dependent on differences in the partial pressure P and the flux equation is

$$F_p = -D_{pm} \cdot \mathrm{grad}\, P \tag{32}$$

D_{pm} is the coefficient for the diffusion of the fumigant in the porous medium soil with P being the dependent variable. The diffusion equation is derived similarly to Equation (7) with the only distinction that there is a changeover from C_g to P by using the ideal gas law.

The explicit difference equation that results for the one-dimensional system is

$$\begin{aligned} P(x, t+\Delta t) = (1-k_r \cdot \Delta t) \cdot \{[1-r_{pm}(xm)-r_{pm}(xp)] \cdot P(x, t)+ \\ +r_{pm}(xm) \cdot P(x-\Delta x, t)+r_{pm}(xp) \cdot P(x+\Delta x, t)\} \end{aligned} \tag{33}$$

In this equation the calculation factors are

$$\begin{aligned} r_{pm}(xm) &= [D_{pm}(xm)/\Phi(x)] \cdot [\Delta t/(\Delta x)^2] \cdot [T(x) \cdot \mathrm{R}/(10^3 \cdot M)] \\ r_{pm}(xp) &= [D_{pm}(xp)/\Phi(x)] \cdot [\Delta t/(\Delta x)^2] \cdot [T(x) \cdot \mathrm{R}/(10^3 \cdot M)] \end{aligned} \tag{34}$$

Coefficient D_{pm} (xm) applies to the diffusion between x and $x-\Delta x$ and $D_{pm}(xp)$ to the diffusion between x and $x+\Delta x \cdot T(x)$ is the temperature in K at position x, M is the molecular weight of the compound, and R is the gas constant.

The comparison of explicit difference Equation (33) with equations (25) and (27), in which C_g is the dependent variable, gives the following relations for r:

$$\begin{aligned} r_{pn}(xm) &= [T(x)/T(xm)] \cdot [D_p(xm)/\Phi(x)] \cdot \Delta t/(\Delta x)^2 \\ r_{pn}(xp) &= [T(x)/T(xp)] \cdot [D_p(xp)/\Phi(x)] \cdot \Delta t/(\Delta x)^2 \end{aligned} \tag{35}$$

$D_p(xp)$ and $D_p(xm)$ are the diffusioncoefficients discussed for the isothermal cases, for the sections x to $x+\Delta x$ and x to $x-\Delta x$, respectively. The consequence of all this for the computations is that the system is more complex which is shown in the calculation of more r-factors. Further P is used as the dependent variable so that the ideal gas law has to be used continually to compute concentrations and doses.

3.8 Changes in conditions with time

Soil fumigation situations occurring in the field are in reality very complex. Changes in conditions with time are generally involved. In the models discussed so far five variables vary with position and time: $P(x, t)$, $D_{pn}(x, t)$, $\Phi(x, t)$, $T(x, t)$ and $k_r(x, t)$. When allowance is made for all these possible variations, the following difference equation is obtained:

$$\begin{aligned} P(x, t+\Delta t) = [1-k_r(x, t) \cdot P(x, t)]\,[(A-r_a-r_b) \cdot P(x, t)+r_a \cdot P(x+\Delta x, t)+ \\ +r_b \cdot P(x-\Delta x, t)] \end{aligned} \tag{36}$$

where

$$A = [\Phi(x, t)/\Phi(x, t+\Delta t)] \cdot T(x, t+\Delta t)/T(x, t)$$
$$r_a = [D_{pn}(xp, t)/\Phi(x, t+\Delta t)] \cdot [\Delta t/(\Delta x)^2] \cdot T(x, t+\Delta t)/T(xp, t)$$

and

$$r_b = [D_{pn}(xm, t)/\Phi(x, t+\Delta t)] \cdot [\Delta t/(\Delta x)^2] \cdot T(x, t+\Delta t)/T(xm, t)$$

The changeover from D_{pn} to D_p can be carried out by using equations (34) and (35) and results in:

$$D_{pn}(xp, t) = \{10^3 \cdot M/[\mathrm{R} \cdot T(xp, t)]\} \cdot D_p(xp, t) \tag{37}$$

In principle, separate values can be introduced and calculated for each point or interval in the imaginary space-time grid. However this requires much time for preparatory calculations and results in extensive computer programmes. In practice, changes with time are only important when they become distinct. Consequently a period with soil fumigation can be divided into a limited number of periods and introduction and realization of changes at some times is satisfactory.

3.9 Calculation of doses

With the value of C_g obtained the dose $B(x)$ is computed for the various positions in the soil profile. If the concentration is changing with time the dose is

$$B(x) = \int_0^{t_f} C_w(x, t)\,\mathrm{d}t \tag{38}$$

$C_w(x, t)$ is the concentration in the water phase and t_f is the point of time at which the computations can be stopped. The concentrations change gradually with time so that the value of the integral can be approximated by the trapezium rule. Combined with $C_w = K_{w/g} \cdot C_g$ the following is obtained:

$$B(x) = \sum_t 0.5 \cdot \Delta t \cdot K_{w/g} \cdot \{C_g(x, t) + C_g(x, t+\Delta t)\} \tag{39}$$

4 Lay-out of field trials and procedures

It was noted in Section 1.5 that there are certain problems with large scale soil fumigation. In the study of 1,3-dichloropropene behaviour in the field, concentrations had to be determined in situ. Samples from various depths were taken at certain times after fumigation. To judge the effectiveness of the fumigations, the complete concentration-time relation for the various depths has to be known. Then the values of the concentration-time integral can be calculated. In practice this requires the analysis of many samples.

The prime object of the computations is to establish whether it is possible to calculate the values of the concentration-time integral from a limited number of concentration measurements. For these computations certain soil characteristics are needed. If these are not available the missing data have to be estimated by a procedure of curve matching between results of calculation and experiment. At the same time information from some field trials is limited. Thus the second object of the computations is to simulate situations for which no measurements were carried out.

4.1 Soil fumigation procedures

Fumigants were applied with the three types of machine currently in use: the tractor-drawn plough injector, subsurface-blade injector and shank injector. In these trials pressure-flow systems were involved in the transport of the liquid from the barrels to the soil. With the plough injector the fumigant is sprayed over the bottom of a furrow, after which a soil layer 15 to 20 cm thick is immediately turned onto it. With the blade injectors a 15 to 20 cm top layer is lifted some centimeters and the liquid is sprayed under the whole breadth of the blade. With the third type of apparatus, shanks are drawn through the soil with tubes behind them that release the fumigant close to the lower end of the shanks.

For prevention a rate of 250 litres per hectare of technical mixture (at least 0.50 g 1,3-dichloropropene per g) is frequently used for soil fumigation. The same amount was used in these trials, unless otherwise stated. The rate was carefully checked by catching the fumigant from the sprayers in a 1 litre graduated cylinder during a known period of normal spraying. If necessary the delivery rates were corrected to obtain equal values for all sprayers. The driving speed of the machines was measured and adjusted to obtain the desired rate. Occasionally during the trials delivery rate and driving speed were checked.

The composition of the technical mixtures was determined occasionally. The average values (deviations were small) were for *cis*-1,3-dichloropropene 0.28 g/g and for *trans*-1,3-dichloropropene 0.26 g/g mixture. After fumigant application, the soil in the top centimeters was crumbled and then firmly rolled with implements normally attached to the injection apparatus. The main field trials were carried out at five places in the Netherlands. Three trials were in the late summer and autumn of 1969 and two in the autumn of 1970. A general description of the trials is given here; the details are given per treatment in Chapter 5.

The first trial was carried out at Oranje in Drenthe on 3 September 1969. The humic sandy soil was rather dry and no rain fell at the site during the first two weeks after fumigation. The temperature at 15 cm depth was 17 °C on the average in this period. The preparation of the soil had resulted in a loose top layer about 7 cm thick. The aim of this trial was to compare the efficiency of soil fumigation equipment. The types used were: a plough injector with drag, the same plough injector with roller, a subsurface-blade injector with roller and a shank injector with roller. An attempt was made to inject at 18 cm depth, but with the blade injector the tractive power was too small and with the shank injector the elastic mounting of the shanks caused a too shallow injection. The size of the plots was 5 × 25 m. Two replicates were sampled. This trial was repeated for other plots at the same field on 15 October 1969. The soil was still rather dry, but soil temperature had decreased to an average of 12 °C at 15 cm depth.

The second trial was carried out at Dedemsvaart in Overijssel. The fumigation took place on 19 September 1969. The plough layer consisted of very humic sand and the organic matter content decreased gradually with depth. The soil was rather dry and the average soil temperature was 14 °C. The main object of this trial was to establish the most suitable time interval before soil turning, to increase fumigation effectivity. The injection was carried out with a shank injector. The distance between the shanks was 25 cm which is exceptional. Usually it is about 18 cm. Beforehand the soil had been loosened to 7 cm depth and the soil beneath this depth was very dense. Both after injection and turning, the soil surface was finished-off by rolling. The plots measured 5 × 10 m. Two replicates were sampled at three intervals after fumigant application.

The third fumigation trial was carried out on 17 October 1969, at a field near Nieuwe Pekela in the Province of Groningen. The soil profile consisted of a peaty sand layer about 13 cm thick on a peat layer, with a sandy subsoil beginning at about 30 cm. The soil was rather dry and the soil had been loosened by tillage to about 9 cm depth. This trial was set up to investigate fumigation of peaty soils, which are hard to fumigate effectively. Both a blade injector and a shank injector were used at two injection depths of approximately 9 and 13 cm. The soil was finished off by rolling. Three replicates were sampled and the plot sizes were 8 × 22 m.

The first trial in 1970 was carried out near Bant in Overijssel on 29 September. The sandy loam (20% of the mineral fraction below 2 μm) was moist. The object of this trial was to investigate the effect of some pretreatments of the soil: deep rototilling and shallow harrowing. After pretreatment the fumigant was applied with a plough injector with a roller attached. The splot sizes at this field were 9 × 30 m.

The fifth soil fumigation trial was carried out on 9 November 1970 at a field near Borgercompagnie in the Province of Groningen. The profile consisted of a peaty sand layer of about 20 cm thickness on a peat layer. This trial was set up to analyse the behaviour of 1,3-dichloropropene in soil under wet conditions. The fumigant was applied with a plough injector and after that the top soil was broken up and rolled. Only one treatment was involved. Five plots at the field were sampled.

The procedures for measurements and computations are discussed in more detail in sections 4.2, 4.3 and 4.4. The emphasis in this report is on the behaviour of 1,3-dichloropropene in soil. The nematode mortalities were determined by scientists from other institutions.

4.2 Determination of 1,3-dichloropropene concentrations in soil

The concentration of *cis* and *trans* 1,3-dichloropropene in soil was determined at different time intervals after the application of the fumigant. The sampling was carried out at five or six different depths with a cylindrical soil auger 3.5 cm in diameter. From the lowest part of the soil core a slice 2 cm thick was taken. Plots were sampled at five randomly selected points and the samples per depth were collected in a glass jar. The jars were immediately closed with a gastight screw cap. The samples were mixed by rotating the jars and then stored overnight at 2 °C.

To 100 ml glass bottles, 20 ml of *n*-hexane and 20 ml of distilled water were added. To prevent evaporation a brass pipe, with a sharp lower end and a bar fitting in it, was used to add quickly 15 g of the soil. The bottles were closed with ground-glass stoppers and shaken mechanically for 2 h. Part of the clear hexane layer was then poured into 10 ml stoppered bottles and diluted if necessary. The concentrations were measured by gas chromatography as outlined in Section 2.1.1.

For each layer the amount recovered was determined by adding known amounts of the isomers of 1,3-dichloropropene to soil from blank plots. For this the same extraction procedure was used, starting with rotating and storing at 2 °C. More than 75% of the fumigant was recovered in all cases, but usually more than 85% was obtained. The extraction procedure given here is similar to that suggested by Smith & Shigenaga (1961) and is suitable for analysing many samples. More complicated procedures reported afterwards did not result in better recovery percentages (Williams, 1968). About 100 samples were analysed per trial.

4.3 Characterization of soil

The bulk density of the soil layers ρ_b was determined from undisturbed soil samples taken with 100 cm^3 stainless steel cylinders. For each treatment at least seven observations per layer were made. For sandy and peaty soil, the organic matter content, *omc*, was estimated by the loss-on-ignition method. At least six mixed samples per layer were analysed. The organic matter content of the loamy soil was estimated by the permanganate oxidation method (de Vries & Dechering, 1960, p. 36). From a large number of measurements on sandy and peaty soils Boekel (1961) found the density of the mineral parts, ρ_{mp}, to be 2.66 g/cm^3 and the density of the organic matter, ρ_{om}, to be 1.47 g/cm^3. The density of the solid phase of the loamy soil was estimated by the picnometer method. The percentage of the mineral parts smaller than 2 µm in the sandy and peaty soils was negligible. The loamy soil contained 20 percent by weight particles smaller than 2 µm, as estimated with the pipette method (de Vries & Dechering, 1960, p. 24).

The soil moisture contents at the various depths after different periods of time were measured by drying the soil to constant weight at 105 °C. For each time interval, at least ten observations per layer were made. In 1 cm^3 of soil the weight of the mineral parts $W_{mp} = \rho_b \cdot (1\text{-}omc)$. Then the volume fraction of the mineral parts $\varepsilon_{mp} = W_{mp}/\rho_{mp}$. For the volume fraction of the organic matter $\varepsilon_{om} = omc \cdot \rho_b/\rho_{om}$. From the moisture content and ρ_b, the volume fraction of the water phase ε_w was calculated. The volume fraction of the gas phase then follows as $\varepsilon_g = 1-(\varepsilon_{mp}+\varepsilon_{om}+\varepsilon_w)$. The values of these physical characteristics for the various layers are given per treatment in the tables in Chapter 5.

4.4 Computation procedures

The procedure for the computations is discussed for the geometrically two-dimensional system with shank injection. The diffusion process can be described in a repeating geometrical unit as represented by Fig. 20. The limits of the soil profile give the upper and lower boundaries. Normally for the soil surface the following boundary condition, standing for a complete sink, is valid:

$$t \geqslant 0 \quad x = 0 \text{ (soil surface) } C_g = 0$$

The boundary condition for the lower end x_e of the soil profile depends on the local situation. Occasionally a complete sink can be assumed:

$$t \geqslant 0 \quad x = x_e \quad C_g = 0$$

This may be a good approximation when the supply of fumigant from above is very slow and the transport downwards is quick, such as when a strongly adsorbing or slightly permeable layer covers a permeable sandy subsoil layer of considerable thickness. The other extreme is the occurrence of an impermeable layer beginning at depth x_e through which positive reflection is obtained. Then

$$t \geqslant 0 \quad x = x_e \quad \partial C_g/\partial x = 0$$

Other boundary conditions for x_e may be included in computations, such as those for dissolution in groundwater at shallow depth.

The two other limits for the geometrical unit are the vertical plane through an injection line ($y = 0$) and the plane in the middle of two adjacent lines ($y = y_e$). The situations at corresponding positions on either side of each of the planes are the same.

So there is complete positive reflection at $y = 0$ and $y = y_e$:

$$t \geqslant 0 \quad y = 0 \quad \partial C_g/\partial y = 0$$
$$t \geqslant 0 \quad y = y_e \quad \partial C_g/\partial y = 0$$

The soil profiles are divided into layers, with the properties important for diffusion and adsorption of fumigants as criteria. The top layer is frequently loose with a dense layer underneath the plough layer. The organic matter content is also a criterion that is often used. The division into layers is based on experimental information available for the entire soil profile.

The next step is to select a suitable space interval $\Delta x = \Delta y$ for the imaginary grid used in the computations. An interval in the range of 2 tot 3 cm was chosen. The exact value is dictated by the geometry of the system. The column of points near the reflection plane at $y = y_e$ can be arranged either through the plane or at a distance of $\Delta y/2$ from the plane.

The volume fractions of the water phase (ε_w) and the gas phase (ε_g) for the layers are calculated from the bulk density, the organic matter content and the moisture content as outlined in Section 4.3. The values of the distribution coefficients $K_{w/g}$ and $K_{s/g}$ at the temperature concerned are obtained from the results given in Section 2.1. With Equation (6) the fumigant capacity factor Φ may then be calculated. The value of the diffusion coefficient D_a follows from Fig. 6. The information on the condition of the various layers is used to estimate the relation between D_p/D_a and ε_g from data reported in literature and obtained for corresponding conditions of the soil samples (Section 2.2.2). After this the value of the diffusion coefficient D_m can be calculated from $D_m = D_p/\Phi$.

The analytical starting solution (equations 21a and b) is used to calculate the concentrations in the grid points at time t_e. To evaluate the exponential function, tables are available such as those of Abramowitz & Stegun (1965, p. 116). After this a time interval Δt is selected that satisfies the condition given in connection with Equation (28). From the values of D_p, Φ, Δt and Δx the calculation factors r used in the difference equations can be derived. Values for r are obtained for each layer and for each array of points near a transition. For the sandy and peaty soils, a low decomposition rate in the range 0.01 to 0.03 day^{-1} is assumed (Section 2.3). The lower limit of the nematicidal active concentrations was supposed to have a low value; for this purpose a concentration was taken that corresponds with $C_w = 2\ \mu g/cm^3$.

The numerical computations were carried out with a Control Data 3200 computer and with an IBM 1130 computer. The programmes were written in FORTRAN. The programme was flexible so that layers and transitions could be inserted or omitted. Computations could then be carried out for a variety of soil situations. Outputs were arranged for different time intervals including those at which concentration was measured. The computations were terminated when the concentrations fell below the lower limit of nematicidal active concentrations.

The computed concentrations were compared with the measured data by graphs. For this purpose the concentration in the water phase C_w was used so that at the same time an impression of the nematicidal activity was obtained. From these comparisons new estimates of D_p, if necessary, were obtained by curve-matching. This procedure is discussed in more detail in Section 5.1. It was necessary to use this procedure because, even after grouping the literature data according to the condition of the soil samples, there was a wide range of estimates for D_p (Section 2.2.2). Once the value of D_p for a layer was established by this procedure, the same value could be used for the other isomer of 1,3-dichloropropene and a good estimate was obtained for related treatments at the trial sites. The doses for the investigated field situations were computed with Equation (39). The computation procedure may be used to assess the significance of application method, soil factors and weather on the fumigation process. In this study simulations were carried out as realistically as possible, usually starting from an investigated field situation and by varying a factor according to the available or approximated basic data. Details are given in Chapter 5.

5 Results and discussion

5.1 Measured and calculated fumigant distributions in prototype situations

First the distribution of *cis* and *trans* 1,3-dichloropropene in soil is discussed on the basis of a number of representative field trials. One of the treatments carried out at the field at Oranje on 15 October 1969, was injection with a plough injector, after which the soil in the upper centimeters was crumbled and rolled (Case 1). At a depth of 18 cm, 250 litres of the mixture (more than 0.50 g dichloropropene per g) was injected per hectare. The humic sandy soil had an average moisture content of 0.13 g/g and the mean temperature was 12 °C. During the first nine days negligible amounts of rain fell at the site. Ploughing resulted in a loose top layer 18 cm thick, under which there was a dense layer passing into a less dense layer. The sandy subsoil was rather dry during fumigation. Details on the composition of the soil and the condition of the layers are given in Table 7.

The amounts of *cis* and *trans* 1,3-dichloropropene, estimated three days after application, are expressed as concentrations in the water phase and represented in Fig. 16. The highest concentrations are still found near the injection depth. Upwards there is a gradual decrease in concentration and the pattern is convex. This indicates that the compounds are disappearing at the soil surface. The concentration gradients are distinctly higher in the layer beneath the injection depth, so that this layer must be more resistant to diffusion than the top layer. At 35 cm depth the concentrations are low.

To compute the concentrations in these plane source situations, the analytical solution Equation 17 and the numerical solutions equations 22, 25 and 27 were used. The basic data in Chapter 2 were used to calculate and estimate the values for the quantities needed in the computations. The values for the fumigant capacity factor Φ follow from the distribution coefficients and the characteristics of the layers (Section 2.1). D_p can be estimated from the results given in Section 2.2. For the ploughed layer the relation between D_p/D_a and ε_g for disturbed samples of moist soil in figs 8 and 9 can be used. The data on the undisturbed samples of moist soil represented in Fig. 10 may be applicable for the layers underneath the injection depth. Thus the following ranges of values for D_p, expressed in $\text{cm}^3/(\text{cm·s})$, are obtained:

layer a (0–18 cm), $\varepsilon_g = 0.38$, D_p range $1.20 \cdot 10^{-2}$ to $1.90 \cdot 10^{-2}$
layer b (18–30 cm), $\varepsilon_g = 0.25$, D_p range $0.31 \cdot 10^{-2}$ to $0.69 \cdot 10^{-2}$
layer c (30–42 cm), $\varepsilon_g = 0.29$, D_p range $0.42 \cdot 10^{-2}$ to $0.80 \cdot 10^{-2}$

These wide ranges may be related to differences within the groups of diffusion data which result from differences in soil type and origin of the samples. For the first computations of the distributions in a soil, values from the middle of these ranges were taken as first approximation. It is hardly surprising that differences were found between the calculated and measured concentrations. Too high estimates for the D_p in the plough layer usually resulted in too low values for the concentrations in this layer because diffusion to the soil surface was overrated. Too high estimates for D_p in layer b usually gave too high values for the calculated concentrations in the lower part of the soil profile. By curve-matching for Case 1, the following approximations of D_p, expressed in $\text{cm}^3/(\text{cm}\cdot\text{s})$, were obtained:

layer a $D_p \approx 1.40 \cdot 10^{-2}$
layer b $D_p \approx 0.39 \cdot 10^{-2}$
layer c $D_p \approx 0.75 \cdot 10^{-2}$

The above approximations fall within the estimation ranges. The concentration pattern, obtained after curve-matching, is given in Fig. 16A.

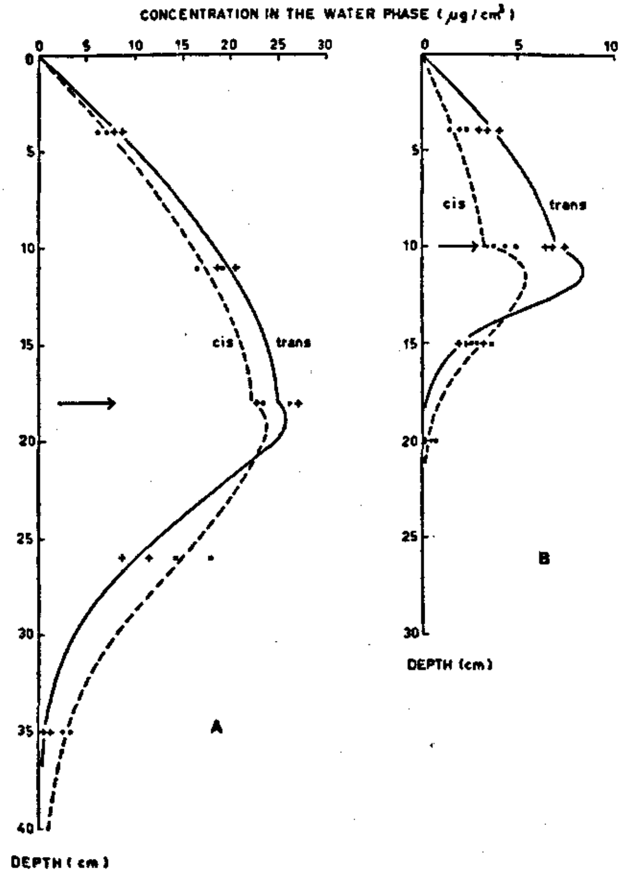


Fig. 16. Concentrations of *cis* and *trans* 1,3-dichloropropene in water phase, some days after application.
A: Case 1, humic sandy soil, 3 days
B: Case 2, peaty sand on peat profile, 5 days
. *cis*, measured
---- *cis*, curve-matching
+ *trans*, measured
— *trans*, curve-matching

The field near Nieuwe Pekela, which was fumigated on 17 October 1969 had a different soil profile. This consisted of a peaty sand top layer about 14 cm thick under which was a peat layer. One of the treatments was blade injection at 10 cm depth of 250 litres of mixture (more than 0.50 g 1,3-dichloropropene per g) per hectare (Case 2). Details of the soil situation are given in Table 7. The amounts of *cis* and *trans* 1,3-dichloropropene, estimated five days after application, are expressed as concentrations in the water phase and are given in Fig. 16B. The D_p ranges inferred from literature data and the approximations of the D_p value from the curve-matching procedure are:

layer a (0–10 cm), $\varepsilon_g = 0.50$, D_p range $1.80 \cdot 10^{-2}$ to $2.50 \cdot 10^{-2}$, $D_p \approx 1.90 \cdot 10^{-2}$
layer b (10–14 cm), $\varepsilon_g = 0.23$, D_p range $0.19 \cdot 10^{-2}$ to $0.61 \cdot 10^{-2}$, $D_p \approx 0.18 \cdot 10^{-2}$
layer c (14–30 cm), $\varepsilon_g = 0.37$, D_p range $0.69 \cdot 10^{-2}$ to $1.10 \cdot 10^{-2}$, $D_p \approx 0.25 \cdot 10^{-2}$

For the top layer the literature data were extrapolated according to Currie (1962, p. 381). The approximation of D_p for the top layer is within the range, but for layer b it is lower. This indicates the high geometrical complexity of the gas-filled pore system in this layer, which is situated underneath the plough layer. For layer c, which is a peat layer still with the original layered structure, a very low value of D_p is found even though there is a considerable volume fraction of gas-filled pores. No diffusion measurements are known for this sort of layer. The estimation ranges for D_p and the approximations obtained by curve-matching are given in the tables in sections 5.2, 5.3, and 5.4.

Approximations of the D_p values for *cis* 1,3-dichloropropene also apply to *trans*-1,3-dichloropropene (Fig. 16). When there are only slight changes in conditions, the concentrations at other sampling times, calculated with the same D_p-approximation, are in good agreement with the measured concentrations. Another point is that, starting from the $D_p/D_a - \varepsilon_g$ relation for one treatment, good estimates can be made for the D_p-values involved with the other treatments at the trial site.

The concentration-depth relations for *cis* and *trans* 1,3-dichloropropene, represented in figs 16A and B, show some interesting features. These are most clearly seen from the results of the calculations. There is a fast rate of disappearance of the fumigant at the soil surface, seen from the concentration gradient in the upper soil centimeters. In Section 2.1 it was shown that the total sorption of *cis*-1,3-dichloropropene from the gas phase was less than that for the *trans* isomer. This means that the fumigant capactity factor for the *cis* isomer is smaller and hence the effective diffusion coefficient D_m is greater. It is clearly shown in Fig. 16 that more *cis*-1,3-dichloropropene has disappeared from the plough layer. On the other hand this greater D_m-value results in a faster penetration of *cis*-1,3-dichloropropene into the denser layers below the injection depth. It is shown in Fig. 16A that a diffusion into deeper layers has already begun. In Fig. 16B the lower limit of the peat layer, situated at 30 cm depth, has not yet been reached.

At transitions between layers with distinctly different values for the diffusion coefficient D_m, definite kinks in the concentration-depth curve occur. This is because a

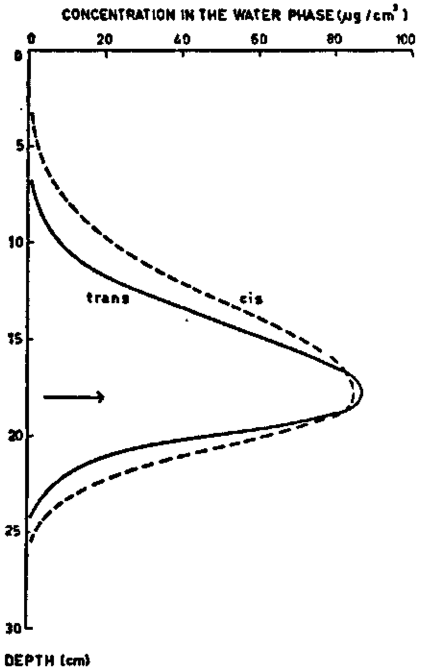


Fig. 17. Concentrations in the water phase of *cis* and *trans* 1,3-dichloropropene 7h after application with a plough injector in humic sandy soil. Computed for Case 1.

higher value of the concentration gradient $\partial C_g/\partial x$ is needed to attain a certain flux F_p in a layer with a lower D_m value. In both figs 16A and 16B, upward diffusion is shown in the top of the layer just below the injection depth. In the last stage of the fumigation the highest concentrations are found at depths greater than the injection depth.

The relations between concentrations and depth, calculated with analytical solution Equation 17 for Case 1 are given in Fig. 17. The time interval after application was 7 h. Because the ploughed layer was considerably looser the amount that diffused upwards (M_1) in the initial period was about 1.8 times the amount that diffused downwards (M_3). The *cis* isomer was spread more than the *trans* isomer because of the weaker total sorption of the former from the gas phase. The total amount of *trans*-1,3-dichloropropene in the water phase was smaller because of the lower percentage of this isomer in the technical mixture and the slightly stronger adsorption onto the solid phase. The low degree of saturation of the fumigant that normally occurs is illustrated by the fact that the highest concentration at the time considered has already fallen to about 0.03 times the saturation concentration (Section 2.1).

The relation between concentration and time for Case 1 is represented in Fig. 18 for two soil depths. The general picture is a rapid increase of the concentration followed by a gradual decrease. Once again the faster diffusion of the more volatile *cis* isomer is shown. In the conditions considered here, which were favourable for diffusion in the gas phase, the concentrations have decreased to low values after two or three weeks. The highest concentrations were then found in the layer underneath the plough layer.

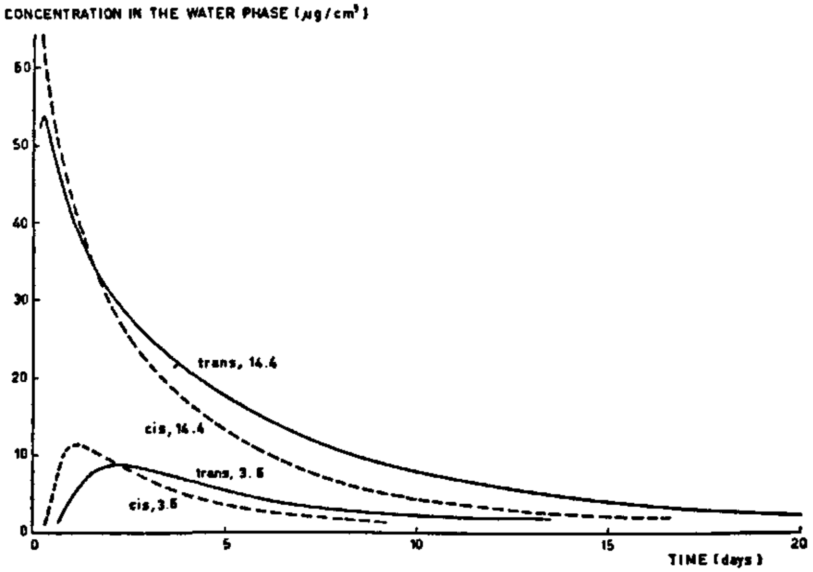


Fig. 18 Relation between concentration in the water phase and time for *cis* and *trans* 1,3-dichloropropene after fumigation of a humic sandy soil, Case 1.
3.6 and 14.4 indicate depths in cm.

In the computations for Case 1, time intervals of 3.6 and 6.1 hours were used for *cis* and *trans* 1,3-dichloropropene, respectively. From Fig. 18 it follows that the concentration-time integral can be evaluated accurately by the trapezium rule (Equation 39). The computed doses B, expressed in (µg/cm³) × day for the isomers at the selected depths of 14.4 and 3.6 cm are B_{cis} (14.4) = 198, B_{trans} (14.4) = 254, B_{cis} (3.6) = 44, and B_{trans} (3.6) = 53. Low values for doses near the soil surface is a general shortcoming of soil fumigation without surface sealing. The value of the dose for the *trans* isomer is at both depths higher than that for the *cis* isomer. On the other hand the nematicidal activity of the *cis* isomer is considerably higher (Section 2.4), so that the contribution of *cis*-1,3-dichloropropene to the mortality of the parasitic nematodes is usually greater than that of *trans*-1,3-dichloropropene.

5.2 Effect of application method

Different machines and the way in which they are used influence the effectivity of soil fumigation. For example a type of shank injector, equipped with 12 shanks elastically fixed at intervals of about 18 cm, often produced comparatively low nematode mortalities. The same holds for a type of plough injector, with rotating knives before the ploughshares, used for loamy soils. With the latter machine the injection depth was usually about 25 cm and the soil surface was left very rough after fumigation.

Sometimes, with other types of machine, the effectivity of fumigation is too low, even under favourable conditions. It is thus necessary to find out whether these difficulties are caused by faults in the construction of the injectors or by shortcomings in the fumigation procedure. This type of information is important both for the use of existing machines and for the development of new fumigation equipment and techniques.

5.2.1 Comparison between types of fumigation equipment

Soil fumigations with various types of equipment were carried out on 15 October 1969. The trial field, situated near Oranje, had a humic sandy soil profile. The machines and combinations involved were: a plough injector (Cases 1 and 3), a blade injector (Case 4) and a shank injector (Case 5). In the Cases 1, 4 and 5 the soil surface was finished off with a roller, whereas in Case 3 a drag was used. A rate of 250 l of mixture, containing at least 0.50 g 1,3-dichloropropene per g, per hectare was applied, except in Case 4 in which the rate was 220 l/ha. Soil temperatures were measured continually after the application and the average temperature at a depth of 15 cm during the first two weeks was 12 °C. The daily fluctuation was between 10 °C and 14 °C and remained fairly constant during this period. During the first nine days negligible amounts of rain fell at the site.

Soil samples for concentration measurements were taken 3 and 14 days after fumigation. The results, expressed as concentrations in the water phase, are given in Table 6. Two plots per treatment were sampled; the results are thus average values of determinations in duplicate. Standard deviations of up to 20% of the average values were found. The concentration patterns give momentary pictures, while the effectivity of a fumigation depends on the dose patterns in the soil. Differences between treatments are therefore discussed on the basis of the doses computed for these situations.

Details on the physical situation after the applications are given in Table 7. The ploughed top layers la and 3a were comparatively loose, as were the intensively tilled top layers 4a and 5a. The layers 4b and 5b were disturbed by the fumigation equipment. The layers just underneath the plough layer had the greatest bulk density. The organic matter content decreased with depth. The soil moisture contents were lower than usual for autumn. The corresponding moisture tension was in the range of pF = 3 (de Vries & Dechering, 1960, p. 143). Accordingly the volume fraction of gas-filled pores was rather high so that the moisture condition was favourable for a rapid distribution of the fumigant in the soil. The estimation ranges for D_p and the approximate values found for these situations by curve-matching are also given in Table 7. In general the approximations for the disturbed layers fall within the ranges, with rather high values for the intensively tilled top layers 4a and 5a. For layer 5b, a somewhat dense layer through which the injection shanks were drawn, D_p is above the estimation range. This may be connected with a preference for diffusion through the looser injection tracks, which constitute only a fraction of the total layer. D_p-values for the layer underneath the plough layer were in the lower part of the estimation ranges. In the deeper layers the diffusion rate was rather high.

Table 6. Concentrations of *cis* and *trans* 1,3-dichloropropene in the water phase.
Cases 1, 3, 4, and 5: 3 and 14 days after fumigation of trial field at Oranje on 15 October 1969.
Case 7: 8 and 16 days after fumigation of field at Dedemsvaart on 18 September 1969.
Time in days, depth in cm, and C_w in µg/cm³.

Time	Compound	Case 1		Case 3		Case 4		Case 5			Time	Case 7	
		Depth	C_w	Depth	C_w	Depth	C_w	Depth	C_w (tracks[1])	C_w (between[2])		Depth	C_w
3	*cis*-1,3 D	4	6.6	4	5.2	4	5.0	3	4.5	4.0	8	5	3.4
		11	18	12	14	10	13	9	15	13		10	8.4
		18	25	19	20	15	19	14	31	23		15	11
		26	16	27	14	25	5.7	24	7.7	4.6		20	4.0
		35	2.9	35	1.8	35	0.3	35	0.2	0.1		25	1.8
												35	0.4
	trans-1,3 D	4	8.3	4	6.3	4	6.0	3	6.2	5.3		5	4.2
		11	19	12	16	10	17	9	23	18		10	11
		18	25	19	21	15	22	14	36	22		15	11
		26	10	27	8.5	25	2.4	24	4.1	1.6		20	2.6
		35	1.1	35	0.8	35	0.1	35	0.0	0.0		25	1.4
												35	0.3
14	*cis*-1,3 D	4	1.8	4	1.6	4	1.5	3	1.1	1.1	16	5	1.3
		11	4.3	12	3.1	10	2.0	9	3.7	3.1		10	3.5
		18	5.8	19	5.1	15	3.7	14	5.5	5.8		15	6.0
		26	6.5	27	4.5	25	4.3	24	4.7	4.6		20	3.8
		35	2.9	35	2.1	35	1.0	35	0.9	0.9		25	1.1
												35	0.2
	trans-1,3 D	4	2.5	4	2.1	4	2.1	3	1.8	2.0		5	2.5
		11	6.8	12	5.1	10	3.7	9	6.0	5.3		10	5.8
		18	8.2	19	7.7	15	5.4	14	8.9	8.0		15	7.5
		26	7.5	27	5.3	25	4.5	24	4.5	4.0		20	3.2
		35	2.1	35	1.7	35	0.6	35	0.4	0.4		25	1.0
												35	0.2

1. Samples taken from injection tracks.
2. Samples taken from midway between injection tracks.

Table 7. Soil physical properties with diffusion and total sorption characteristics for *cis* and *trans* 1,3-dichloropropene. Comparison of soil fumigation apparatus and overlap of the dose patterns after shank injection.

Case	Layer or part	Depth (cm)	ρ_b (g/cm^3)	*omc* (g/g)	ε_w (cm^3/cm^3)	ε_g (cm^3/cm^3)	D_p (cm^3/(cm · s); ×100)		Φ (cm^3/cm^3)	
							estimation range	approximated value	*cis*	*trans*
1	a	0–18	1.22	0.055	0.15	0.38	1.20–1.90	1.40	30	53
	b	18–30	1.42	0.049	0.20	0.25	0.31–0.69	0.39	33	57
	c	30–42	1.40	0.037	0.17	0.29	0.42–0.80	0.75	25	43
2	a	0–10	0.68	0.18	0.20	0.50	1.80–2.50	1.90	56	93
	b	10–14	1.00	0.18	0.34	0.23	0.19–0.61	0.18	84	138
	c	14–30	0.48	0.95	0.31	0.37	0.69–1.10	0.25	204	338
3	a	0–19	1.18	0.055	0.14	0.40	1.40–2.10	1.87	29	51
	b	19–30	1.42	0.049	0.20	0.25	0.31–0.69	0.40	33	57
	c	30–42	1.40	0.037	0.17	0.29	0.42–0.80	0.75	25	43
4	a	0– 7.5	1.17	0.055	0.14	0.40	1.40–2.10	1.90	29	51
	b	7.5–15	1.30	0.055	0.17	0.32	0.65–1.30	1.00	32	57
	c	15–30	1.43	0.050	0.20	0.24	0.23–0.65	0.28	33	58
	d	30–42	1.40	0.037	0.17	0.29	0.42–0.80	0.75	25	43
5	a	0– 7	1.23	0.055	0.14	0.38	1.20–1.90	1.90	30	53
	b	7–14	1.40	0.055	0.18	0.27	0.34–0.92	1.15	35	61
	c	14–30	1.44	0.050	0.20	0.23	0.19–0.61	0.30	33	58
	d	30–42	1.40	0.037	0.17	0.29	0.42–0.80	0.75	25	43
6	a	0– 7.5	1.23	0.055	0.14	0.38		1.90	30	
	b	7.5–15	1.42	0.055	0.19	0.26		0.48	35	
	c	15–30	1.44	0.050	0.20	0.23		0.30	33	
	d	30–42	1.40	0.037	0.17	0.29		0.75	25	
7	a	0– 7.5	1.01	0.145	0.23	0.35	0.90–1.70	1.80	65	
	b	7.5–15	1.22	0.145	0.32	0.16	0.08–0.38	0.23	80	
	c	15–25	1.40	0.090	0.29	0.14	0.04–0.31	0.11	59	
	d	25–40	1.62	0.036	0.20	0.17	0.12–0.46	0.23	29	

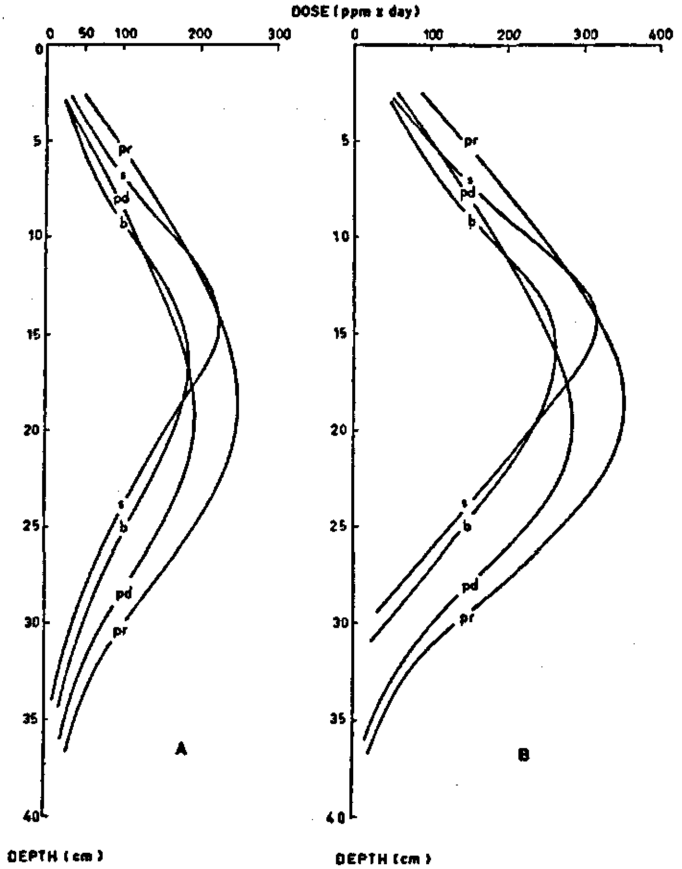


Fig. 19 Doses achieved by fumigating humic sandy soil with various types of machines.

A = *cis*-1,3-dichloropropene B = *trans*-1,3-dichloropropene
pr = plough injector+roller (Case 1)
pd = plough injector+drag (Case 3)
b = blade injector (Case 4)
s = shank injector (Case 5)

The doses computed for these situations are represented in Fig. 19. The computations were checked for the two sampling times, 3 and 14 days after fumigant application. The rate in Case 4 (line b) was 220 l/ha whereas in the other cases it was 250 l/ha. Differences between the treatments were enhanced by the rain that fell nine days after application. The effect of rainfall is discussed separately in Section 5.3.5.

First the two applications with a plough injector are considered. The diffusion rates for the isomers of 1,3-dichloropropene were decreased by rolling. This is especially favourable when the soil is rather dry and the diffusion rate is high, as was the case here. As a result higher doses were achieved at the various depths. The most important practical aspect of rolling is that it reduces the thickness of the top layer, in which the doses are too low for a satisfactory control of parasitic nematodes.

With the use of shank injectors dose patterns around the injection lines should overlap so that the nematodes are uniformly controlled at all depths. For Case 5 additional concentration measurements were carried out for soil samples taken from midway between the injection tracks. The results are included in Table 6. Three days after fumigation, the concentrations between the tracks were considerably lower. After two weeks, however, they did not differ significantly from the concentrations near the tracks. To study the consequences of this slow penetration on the dose patterns in soil, detailed computations were carried out (Section 5.2.2.). Now the average positions of the important iso-dose lines are compared with that for the other machines.

The injection depths with the blade and shank injection were 15 and 14 cm, respectively. Injection could not be deeper because the fumigation equipment had a great working width and the available tractive power was comparatively small. From Fig. 19 it can be seen that although injection was shallow, the doses in the upper centimeters of the soil were not high. Penetration in the layers underneath the plough layer was distinctly less than with deeper injection.

In Section 2.4 it was found that the dose range of 50 to 100 ppm × day is critical. With the plough injector plus roller, the layer with low doses is comparatively thin. If rolling is omitted the result is unfavourable for top layer fumigation. The concave pattern for the dose lines in the top layers with the blade and shank injection would be expected for injection in a denser layer, with a looser layer just underneath the soil surface. Apparently the partial sealing of the soil surface by rolling was not very effective with the blade and shank injectors. The residues of stubble present in the top centimeters decreased effectiveness.

Comparison of soil fumigation machines is a complex matter. Probably if equal rates of fumigant are applied there is little difference in effectivity between plough injector plus drag, blade injector plus roller, and shank injector plus roller in the situation considered. For possible causes for differences in effectivity, secondary factors like structure of layers, injection depth and condition of the soil surface should be studied. Detailed information on several aspects of soil fumigation is needed to judge the quality of the work done with different soil fumigation equipment.

5.2.2 Overlap of dose patterns with shank injection

Only when the dose patterns around the injection lines overlap sufficiently, can nematode mortality be equivalent to that for plough and subsurface-blade injectors. The question is under what conditions does sufficient overlap occur and whether tillage is needed to obtain the right conditions. Simulation computations were set up, mainly based upon the situations at the trial sites at Oranje (humic sand, Case 6) and Dedemsvaart (very humic sand, Case 7) in the autumn of 1969. The layer 0–7.5 cm was loosened by tillage. The injection tracks were assumed to be 3 cm wide, 7.5 cm deep, and filled with material having the same properties as that of the top layer. Between the tracks there was denser soil, undisturbed by the injection shanks. The

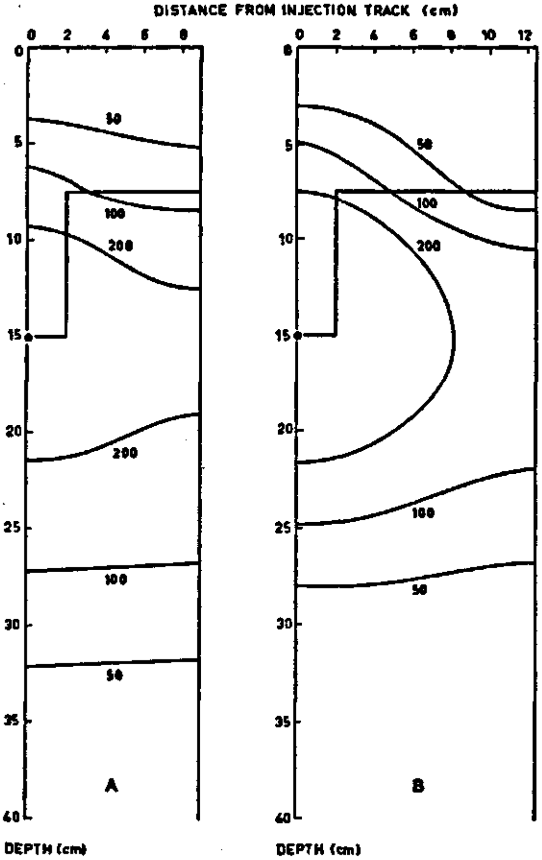


Fig. 20. Overlap of dose patterns with shank injection which gives loose injection tracks with denser soil parts between them.
A = Case 6, B = Case 7
50, 100, and 200 = doses for *cis*-1,3-dichloropropene in the water phase (ppm × day).

physical properties of the soil sections for Cases 6 and 7 are given in Table 7. The soil moisture was favourable for diffusion in the gas phase. There were considerable differences between the D_p-values for the tracks and the denser soil sections. The computations were carried out for *cis*-1,3-dichloropropene at 12 °C. For the numerical computations a grid was used with an interval of $\Delta x = \Delta y = 1.5$ cm.

The computed doses for Case 6 are given in Fig. 20A. The doses above the tracks are somewhat higher than those midway between the tracks. There is a shade effect of the denser soil parts so that fumigation of the soil behind the denser soil is more difficult. Nevertheless the overlap of the iso-dose lines in the important range of 50 to 100 ppm × day is fairly good. The pattern of the iso-dose lines for Case 7, represented in Fig. 20B, is less favourable. There is strong undulating dose-distance relation with an amplitude of about 5 cm for the most important lines. The main reason for this unfavourable pattern is the great distance between the injection shanks, which was 25 cm in this case.

When the distance between the shanks is not too great, problems are of the same nature as that for the other types of soil fumigation equipment. For shank injection the finishing off may be difficult, for example when many plant residues are present. These interfere with the complete filling of the injection grooves with soil and with the partial sealing of the soil surface by rolling. As a result the fumigant will escape quickly. Because the penetration in dense soil sections is a slow process, much of the fumigant will have disappeared before considerable penetration takes place. The overlap of the dose patterns will then be worse than in Case 6.

Although the overlap of the dose patterns is fairly good the injection in dense layers after shallow soil preparation does not necessarily give optimum results. To study this, comparisons should be made with procedures like plough injection, blade injection, and ploughing till injection depth before shank injection. A general discussion of soil structure effects is given in Section 5.3.4.

5.2.3 Injection depth

In practice there is a tendency to use fumigation equipment with a great working width but the tractive power may be insufficient for a satisfactory injection depth. Sometimes very deep injection does occur. To investigate the optimum range of injec-

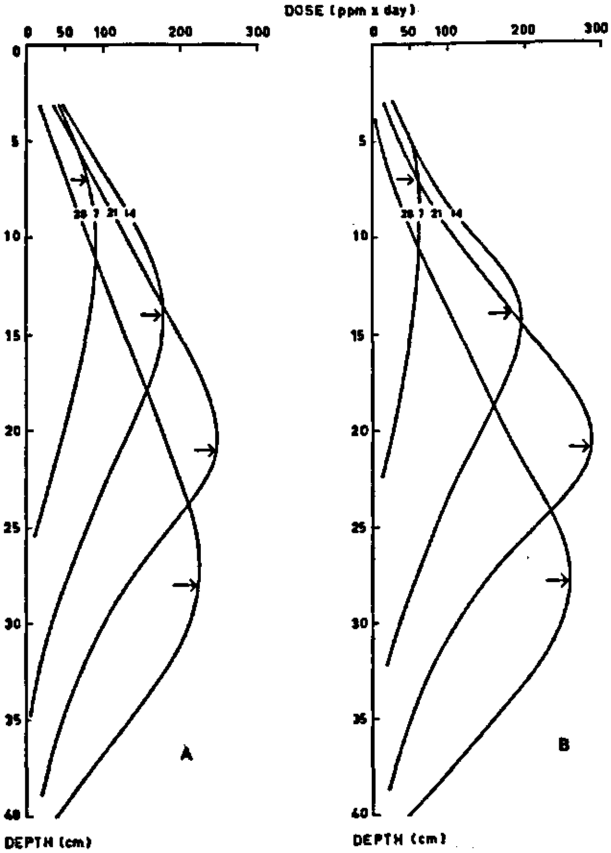


Fig. 21. Effect of injection depth on doses obtained for *cis*-1,3-dichloropropene in a humic sandy soil. Injection depths 7, 14, 21, and 28 cm
A = Cases 8, 9, 10, and 11
B = Cases 12, 13, 14, and 15

tion depths and the reasons for poor results with too shallow or too deep injection, a series of computations were carried out for injection depths of 7, 14, 21 and 28 cm (Cases 8, 9, 10 and 11). The soil concerned was humic sandy and fumigated with a plough injector. The starting point of the computations was the situation after plough-injection plus rolling at the field at Oranje (Case 1). The assumed physical characteristics of the layers are represented in Table 8. The computations were carried out for *cis*-1,3-dichloropropene; for the *trans* isomer the same general picture is to be expected. The computed doses are given in Fig. 21A.

With shallow injection at 7 cm depth only low doses were achieved. There is a quick discharge to the soil surface. This results in low values of the concentration-time integral and in poor penetration to deeper layers. Therefore a large section of the soil with possibly high nematode densities is insufficiently fumigated. With this shallow injection, even the top centimetres are not better fumigated than with the in-

Table 8. Computations on dose patterns with injection at different depths. Division in layers and soil physical characteristics.

Case	Layer	Depth (cm)	ρ_b (g/cm^3)	*omc* (g/g)	ε_w (cm^3/cm^3)	ε_g (cm^3/cm^3)	D_g (cm^3/(cm · s); ×100)	Φ, *cis*-1,3 D (cm^3/cm^3)
8	a	0– 7	1.22	0.055	0.15	0.38	1.40	30
	b	7–14	1.40	0.055	0.18	0.27	0.50	35
	c	14–30	1.43	0.050	0.20	0.24	0.28	33
	d	30–42	1.40	0.037	0.17	0.29	0.75	25
9	a	0–14	1.22	0.055	0.15	0.38	1.40	30
	b	14–30	1.43	0.050	0.20	0.24	0.28	33
	c	30–42	1.40	0.037	0.17	0.29	0.75	25
10	a	0–21	1.22	0.055	0.15	0.38	1.40	30
	b	21–30	1.43	0.050	0.20	0.24	0.28	33
	c	30–42	1.40	0.037	0.17	0.29	0.75	25
11	a	0–28	1.22	0.055	0.15	0.38	1.40	30
	b	28–42	1.40	0.037	0.17	0.29	0.75	25
12	a	0– 7	1.17	0.055	0.14	0.40	1.90	29
	b	7–14	1.40	0.055	0.18	0.27	0.50	35
	c	14–30	1.43	0.050	0.20	0.24	0.28	33
	d	30–42	1.40	0.037	0.17	0.29	0.75	25
13	a	0– 7	1.17	0.055	0.14	0.40	1.90	29
	b	7–14	1.30	0.055	0.17	0.32	1.00	32
	c	14–30	1.43	0.050	0.20	0.24	0.28	33
	d	30–42	1.40	0.037	0.17	0.29	0.75	25
14	a	0– 7	1.17	0.055	0.14	0.40	1.90	29
	b	7–21	1.30	0.055	0.17	0.32	1.00	32
	c	21–30	1.43	0.050	0.20	0.24	0.28	33
	d	30–42	1.40	0.037	0.17	0.29	0.75	25
15	a	0– 7	1.17	0.055	0.14	0.40	1.90	29
	b	7–21	1.30	0.055	0.17	0.32	1.00	32
	c	21–28	1.33	0.050	0.19	0.30	0.80	31
	d	28–42	1.40	0.037	0.17	0.29	0.75	25

jection at 14 cm.

Too great an injection depth, here 28 cm, also seems unfavourable. The doses in the deeper layers are high but this is at the cost of the fumigation in the upper centimetres of the soil. This 'escape' layer is about twice as thick as with injection at 14 cm depth. The two main causes are that more of the fumigant diffuses downwards from the injection depth and that the concentrations at greater distances from the injection position are always lower.

The optimum range of injection depths is apparently 15–20 cm. With an injection depth of 14 cm, the penetration in deeper layers is still poor. With 21 cm the badly-fumigated top layer becomes noticeable thicker. The results of these computations agree with results obtained by measuring nematode mortality at various depths. It now becomes clear that differences in doses, obtained for the various soil fumigation equipment represented in Fig. 19, can be partly attributed to differences in injection depth.

For comparison, results are also given for a series of computations (Cases 12, 13, 14 and 15, cf. Fig. 21B), based on a blade injection situation (Case 4). Again the doses of *cis*-1,3-dichloropropene were computed. The relevant physical properties of the layers are given in Table 8. An important difference from the preceding series is that with this blade injection rolling was less effective, because of the loose soil and the stubble residues in the top centimetres. This can also be inferred from the concave dose pattern in the upper centimetres shown in Fig. 19. With these blade injections there is a comparatively thick top layer that is insufficiently fumigated (cf. Fig. 21B). Furthermore the penetration below the injection depth with shallow injection is poorer than with a more firmly compressed soil surface. The combination of shallow injection and faulty aftertreatment is especially unfavourable.

5.3 Soil composition and condition

It is not easy to control soil-borne pathogens like parasitic nematodes. These parasites occur at various depths, with the highest populations usually in the upper part of the soil. Thus the top of the soil profile must be well fumigated. On the other hand an adequate working-depth is required to prevent dense populations rapidly building up again in the whole root zone. The volatility of a nematicidal compound is important when a large amount of soil is disinfected. The concentration-time relation of the fumigant at various positions in the soil depends strongly on soil composition and structure conditions. As far as the composition is concerned the organic matter content and the buil-up of the soil profile are probably most important. In practice various types of sandy, peaty and loamy soils are involved in large-scale fumigation. With each application much soil preparation and finishing off is involved so that costs may increase considerably. For effective fumigation the structure of the soil and the acceptability of clods and cracks should be investigated.

Table 9. Soil physical properties with diffusion and adsorption characteristics for *cis* and *trans* 1,3-dichloropropene. Shank injection in a peaty soil (Case 16). Isolated effect of soil organic matter content (Cases 17, 18 and 19). Comparison between two types of tillage for a sandy loam (Cases 21 and 22). Effect of clods in the plough layer (Cases 23 and 24). Condition of the soil surface (Cases 28, 31 and 32).

Case	Layer or part	Depth (cm)	ρ_b (g/cm^3)	*omc* (g/g)	ε_w (cm^3/cm^3)	ε_g (cm^3/cm^3)	D_p (cm^3/(cm · s); × 100)		Φ (cm^3/cm^3)	
							estimation range	approximated value	*cis*	*trans*
16	a	0– 9	0.77	0.18	0.21	0.46	1.70–2.30	1.70	63	104
	b	9–13	0.98	0.18	0.32	0.25	0.31–0.69	0.21	81	133
	c	13–30	0.48	0.95	0.31	0.37	0.69–1.10	0.25	204	338
17	a	0–18	1.22	0.055	0.16	0.36		1.32	31	53
	b	18–30	1.42	0.049	0.20	0.25		0.36	33	57
	c	30–42	1.40	0.037	0.17	0.29		0.71	25	44
18	a	0–18	1.11	0.18	0.16	0.36		1.32	86	144
	b	18–30	1.30	0.16	0.20	0.25		0.36	89	151
	c	30–42	1.31	0.12	0.17	0.29		0.71	69	116
19	a	0–18	0.90	0.18	0.25	0.36		1.32	73	122
	b	18–30	1.08	0.16	0.29	0.25		0.36	78	131
	c	30–42	1.10	0.12	0.26	0.29		0.71	61	102
21	a	0–21	1.11	0.025	0.22	0.34	0.81–1.50	1.36	17	29
	b	21–30	1.43	0.022	0.31	0.13	0.04–0.31	0.23	21	35
	c	30–42	1.40	0.016	0.28	0.18	0.12–0.46	0.39	17	28
22	a	0–18	1.18	0.025	0.24	0.29	0.46–1.10	0.98	18	31
	b	18–30	1.43	0.022	0.31	0.13	0.04–0.31	0.23	21	35
	c	30–42	1.40	0.016	0.28	0.18	0.12–0.46	0.39	17	28
23 & 24	clod	0– 8	1.46	0.025	0.33	0.09		0.12	23	29
	loose	0–18	1.14	0.025	0.26	0.29		1.16	19	31
28	a	0– 4.8	1.33	0.055	0.16	0.32		1.08	33	
	b	4.8–19	1.18	0.055	0.14	0.40		1.87	29	
	c	19–30	1.42	0.049	0.20	0.25		0.40	33	
	d	30–42	1.40	0.037	0.17	0.29		0.75	25	
31 (2nd period)	a	0– 6	1.22	0.055	0.40	0.13		0.19	34	
31 (3rd period)	a	0–18	1.22	0.055	0.23	0.29		1.00	32	
32 (2nd period)	a	0– 6	1.22	0.055	0.40	0.13		0.077	34	
32 (3rd period)	a	0–18	1.22	0.055	0.23	0.29		0.385	32	

5.3.1 Fumigation of a peaty soil

The trial field near Nieuwe Pekela was fumigated on 17 October 1969. The soil consisted of a thin layer of peaty sand, about 13 cm thick, over a peat layer. The organic matter content of the soil was so high that is was doubtful whether the nematodes could be satisfactorily controlled with the doses for humic sandy soils. The optimum range of injection depths for most soils (15–20 cm) is in the peat layer.

The fumigations were carried out with a blade injector (Case 2) and with a shank injector (Case 16). The effective rate was 250 liters of mixture, containing at least 0.50 g 1,3-dichloropropene per g, per hectare. The injection depths in the cases 2 and 16 were 10 and 9 cm, respectively. The average temperature at 10 cm depth was 12 °C. During the first seven days the amounts of rain at the site were of no importance (the effect of rainfall is discussed in Section 5.3.5). The physical characteristics of the soil are given in tables 7 and 9. The organic matter content of the top layer was high (0.18 g/g) and the bulk densities, in particular that in the upper part of the top layer, were low. This resulted from intensive tillage of the upper 9 cm of soil in rather dry conditions. As a result the volume fraction, ε_g, of the gas-filled pores was high. In the peat layer, beginning at a depth of about 13 cm, the original layered structure was still found. At depths greater than 30 cm there was a sandy layer that was also rather dry because of the small amounts of rain in the preceding months.

Concentrations of *cis* and *trans* 1,3-dichloropropene in soil were determined 5 and 13 days after application. The concentrations in the water phase at different depths are given in Table 10. After 5 days the concentrations were already low. The concentrations in the peat layer were continuously low and penetration was very limited. The *cis* isomer, which is more volatile in soil, disappeared more quickly from the top layer and penetrated somewhat faster into the peat layer.

In Fig. 22 the doses for *cis* and *trans* 1,3-dichloropropene are given. The higher doses for the *trans* isomer, resulting from the lower diffusion rate, are clearly shown.

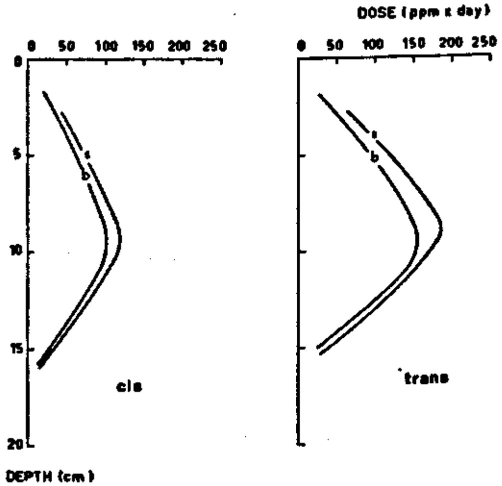


Fig. 22. Doses of *cis* and *trans* 1,3-dichloropropene obtained with fumigation of a peaty soil.
b = blade injection (Case 2). Injection depth 10 cm.
s = shank injection (Case 16). Injection depth 9 cm.

Table 10. Concentrations of *cis* and *trans* 1,3-dichloropropene in water phase. Cases 2 and 16: 5 and 13 days after fumigation of peaty soil at Nieuwe Pekela. Cases 21 and 22: 2 and 7 days after fumigation of sandy loam at Bant.

Time	Compound	Case 2		Case 16		Time	Case 21		Case 22	
		Depth	C_w	Depth	C_w		Depth	C_w	Depth	C_w
5	*cis*-1,3 D	4	1.9	4	2.0	2	5	5.3	5	6.8
		10	4.3	9	4.5		10	15.6	10	17.5
		15	3.0	14	4.0		15	22.3	15	24.4
		20	0.4	19	0.5		20	27.5	20	27.5
		26	0.0	25	0.0		30	15.7	30	3.8
	trans-1,3 D	4	3.5	4	3.7		5	7.1	5	8.8
		10	6.8	9	7.5		10	20.6	10	22.8
		15	2.6	14	4.6		15	27.5	15	30.4
		20	0.2	19	0.3		20	35.6	20	28.4
		26	0.0	25	0.0		30	12.6	30	1.3
13	*cis*-1,3 D	4	1.1	4	1.2	7	5	0.6	5	1.4
		10	1.9	9	2.2		10	2.0	10	3.1
		15	1.7	14	2.0		15	4.3	15	5.0
		20	0.5	19	0.9		20	6.4	20	6.2
		25	0.1	25	0.1		30	9.6	30	3.1
	trans-1,3 D	4	2.1	4	2.2		5	1.3	5	3.3
		10	3.2	9	4.1		10	4.2	10	6.6
		15	1.9	14	2.3		15	8.9	15	9.1
		20	0.3	19	0.4		20	12.3	20	8.7
		25	0.0	25	0.1		30	10.6	30	1.8

The doses were somewhat higher with shank injection, because the upper part of the top layer was loosened less than in the blade injection trial. There was a very quick upward diffusion as a result of the higher volume fractions of gas-filled pores. This diffusion, together with the shallow injection depth (Section 5.2.3) and the poor sealing of the loose and dry top layers, resulted in a rapid escape of the fumigant at the soil surface. The high diffusion resistance resulted in low doses in the layer underneath the injection depth. In the peat layer the diffusion was also slow although the volume fraction of gas-filled pores was 0.37. There was furthermore a strong adsorption in the peat layer which gave high Φ-values (tables 7 and 9). The limitation of appreciable doses to the upper part of the peat layer resulted from both the adsorption and diffusion properties of this layer.

The trial discussed in this section was carried out at two injection levels; about 9 cm and about 13 cm. The injection depths of about 13 cm coincided approximately with the upper limit of the peat layer. From the concentration measurements it followed that the distribution of the fumigant was very uneven. With higher soil moisture contents, which normally occur in autumn, this distribution will be even more unfavourable (Section 5.4.4). Then parts of the soil with possibly high nematode densities, receive low fumigant doses. When the average values of the measured concentrations for the deeper injection levels were compared with those for shallower injection, the doses in the upper centimeters of the soil were slightly higher. This was so because there was more fumigant present when it rained. In the upper part of the peat layer the doses were higher, but at depths greater than 22 cm there were no significant doses.

With injection of fumigants in the peat layer there is a great risk that there will be considerable amounts of fumigant over long periods (Section 6.2). Shallow injection, however, has the disadvantage that the rate of escape of the fumigant at the soil surface is too high (Section 5.2.3). With this type of situation it is best to inject a few centimeters above the transition to the peat layer.

It is interesting to compare the doses represented in Fig. 22 with those obtained for humic sand soil given in Fig. 19. With the humic sand soil the maximum doses were about twice as high. In both situations, however, there was a layer of some centimeters just underneath the soil surface, that was insufficiently fumigated. From the nematode mortality percentage-dose relationship it follows that the thickness of the layer that receives too low doses will not differ very much in the two situations.

From Fig. 22 it seems that the doses near the transition to the peat layer were sufficient to obtain a good mortality percentage. The mortality percentage for this type of peaty soil will be lower because the layer in which the nematodes escape from the treatment forms a greater part of the sampled top layer.

The situations discussed in this section were special cases with respect to organic matter content, injection depth and structure condition. For the development of more general conclusions it is necessary to consider these factors separately.

5.3.2 Isolated effect of soil organic matter content

The organic matter content of fumigated soils may vary considerably. From the measurements discussed in Section 2.1 it follows that the adsorption of the isomers of 1,3-dichloropropene in soil is roughly proportional to the organic matter content. Strong adsorption causes low concentrations in the water phase so that the nematicidal activity is comparatively low. Thus soils high in organic matter content are difficult to fumigate effectively. Questions arise on the extent of the differences in doses and on the supplementary amounts of fumigant that have to be applied to obtain doses comparable with those for soils with low organic matter content.

To study the isolated effect of soil organic matter content, simulation runs were made. The fumigation of a humic sandy soil (5.5% (w/w) organic matter) at 12 °C was taken as reference situation (Case 17). The doses are given in Fig. 23. In Case 18 the only primary factor changed was the soil organic matter content. This was enlarged to 18% (w/w) for the plough layer, while a gradual decrease with depth, similar to that for the sandy soil, was taken. The specifications for this situation are given in Table 9. The computed doses are represented in Fig. 23.

From the adsorption data alone, doses about one third of those for sandy soil are to be expected. However the difference in doses was much smaller. A second impor-

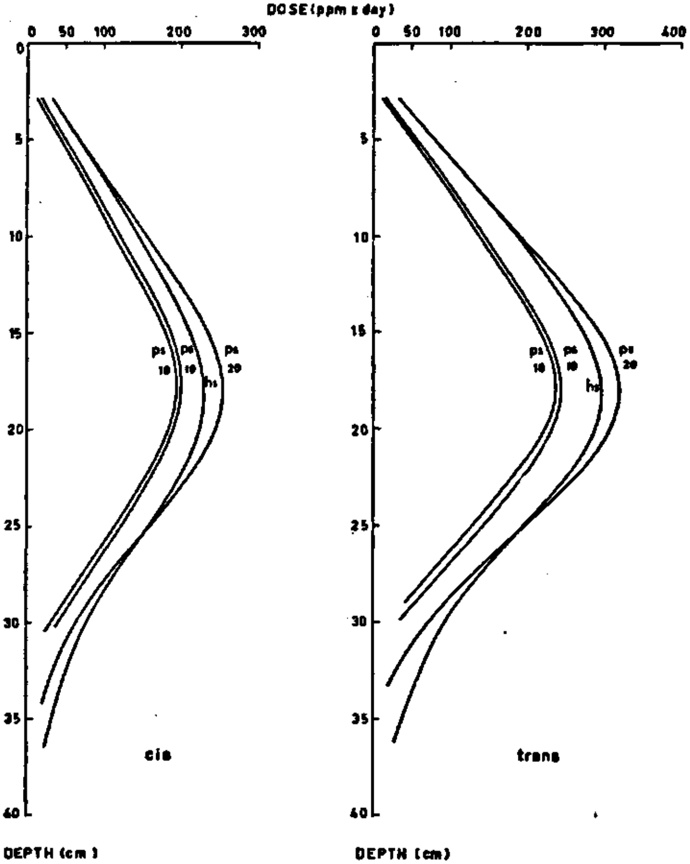


Fig. 23 Simulation series on the effect of soil organic matter content on doses for *cis* and *trans* 1,3-dichloropropene.
hs = humic sand, Case 17
ps = peaty sand, Cases 18, 19, and 20 respectively

tant factor is the diffusion rate, which is low when the organic matter content is high. This largely compensates for the effect of the lower concentrations in the water phase. From Fig. 23 it follows that the difference in nematode mortality is connected with the thickness of the insufficiently fumigated top layer.

The differences in practice between the doses for humic sands and peaty sands can be better estimated by taking into account the lower bulk densities and the higher moisture contents of the peaty sands (de Vries & Dechering, 1960). In Case 19 the bulk density was lowered and the moisture content increased. This was done in such a way that the diffusion coefficient D_p was equal to that in Case 18. See Table 9. From the results for Case 19 given in Fig. 23 it follows that the doses are only slightly higher than those in Case 18.

To investigate the rates needed in Case 19 to obtain doses in the critical soil zones comparable with those for the humic sandy soil (Case 17), computations were carried out for the situation in Case 19, but with higher rates. The fumigation efficiency will be equivalent in Case 20, in which a rate was taken 1.25 times that for Case 17. For the final conclusion on the rates needed for peaty sand soils, other factors besides the organic matter content have to be considered.

When the soil surface is sealed after fumigant application, for example with plastic sheeting, the diffusion rate is less important and differences are related more to adsorption. Here differences in rates or exposure times for a certain control in sandy and peaty soils are much greater, as was established in horticulture for chloropicrin and methyl bromide.

5.3.3 Comparison between two types of tillage for a sandy loam

The fumigation of a sandy loam soil was investigated at a trial site near Bant. Two types of soil preparation were involved: deep rototilling (Case 21) and shallower rotatorharrowing (Case 22). The rototilling resulted in very loose soil; after harrowing part of the top soil was unchanged. On 29 September 1970, the fumigant was applied with a plough injector at a rate of 300 litres of mixture, containing at least 0.50 g 1,3-dichloropropene per g, per hectare. The injection depth was 21 cm in Case 21 and 18 cm in Case 22. The soil was finished-off by rolling, but afterwards there were still cracks in the soil surface. The relevant physical properties of the soil layers, during the first days after fumigation, are given in Table 9. The average temperature at 15 cm was 12 °C with daily fluctuations of about 2 °C. During the first two days after fumigant application the conditions were favourable for a rapid distribution of the fumigant through the soil. In the next five days, 35 mm of rain fell at the site, followed by a period of about 10 days with practically no rain.

The concentrations of *cis* and *trans* 1,3-dichloropropene were measured 2 and 7 days after application of the fumigant. The sampling was carried out in quadruplicate. The average values for the concentration in the water phase at the different depths are given in Table 10. The range of standard deviations was up to 18 % of the average values in this situation. Two days after application the fumigant was well distributed in the soil profile. With the greater injection depth (Case 21) there was a better penetration into deeper layers. In Case 22, in which the soil was less intensively prepared, a more favourable concentration-time relation was found in the top centimeters of the soil. Computations were also set up for these situations. It turned out that the disappearance rate was considerably higher than would follow from the diffusion rates together with a low decomposition rate. The most probable cause is that the decomposition rate is high. This phenomenon for loamy soils, is discussed in more detail in Section 6.4. By comparing the results from the computations and the concentration measurements it could be inferred that the decomposition rate constant k_r had presumably a value in the range of 0.20 day^{-1}. Because the decomposition rate was high in this situation, the doses could only be calculated approximately. The doses estimated for the two types of tillage are represented in Fig. 24. A serious consequence of the high decomposition rate was that a large amount of the fumigant

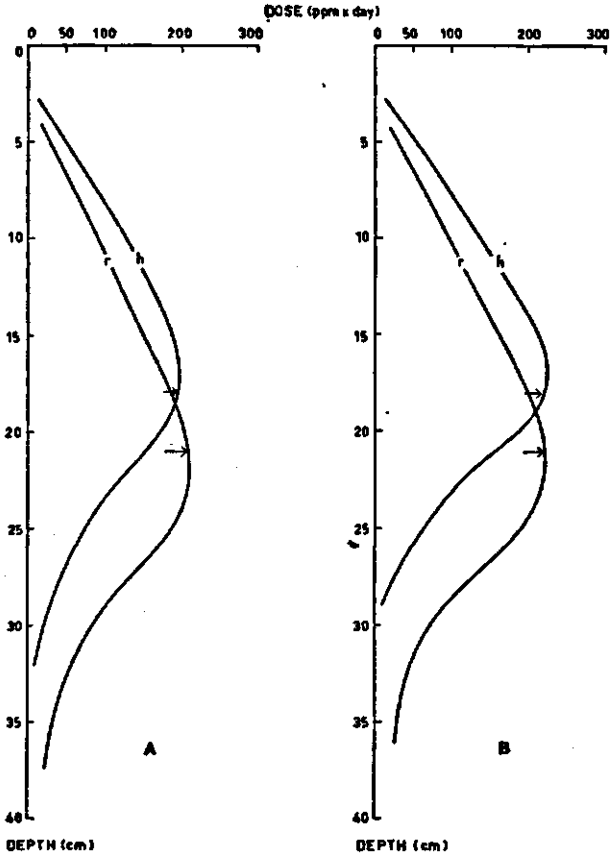


Fig. 24. Approximate values of doses for 1,3-dichloropropene obtained with the fumigation of a sandy loam with a plough injector.

A = *cis*-1,3-dichloropropene B = *trans*-1,3-dichloropropene

r = preparation by rototilling, Case 21

h = preparation by harrowing, Case 22

was decomposed before the critical zones were reached. Because of this there was a thick layer underneath the soil surface in which only low doses have been achieved. From test computations it follows that with a low decomposition rate the doses here would have been more than double. For the plots prepared by rototilling, the doses in the top layer were distinctly lower than those for the harrowed plots. This results from the greater injection depth, the looser topsoil and the many cracks in the soil surface that remained after rolling the rototilled soil.

5.3.4 Effect of clods in the plough layer

An important question is how intensively the soil has to be prepared to obtain an acceptable dose pattern with dichloropropene fumigation. At one extreme preparation can be omitted, at the other the soil can be rototilled up to injection depth. With rototilling the cost of fumigation is increased and unfavourable structure and moisture conditions may develop in the following spring. In this section the influence of clods in a plough layer is studied and a maximum permissable clod size is estimated.

One of the soil preparations at the trial field near Bant (20% clay) was rotator harrowing, by which a layer about 9 cm thick was loosened. After fumigant application with the plough injector, there were clods from the unprepared section of the plough layer (Case 22). To obtain an impression of concentration differences within the clods, soil from outside and inside a clod was collected separately. The centres of the clods were situated at depths of about 5 cm and 10 cm, respectively. The samples were taken from a central slice 2 cm thick. The diameters of the clods were in the range 5–10 cm. Four plots of the trial site were sampled. Four clods from each depth were sampled per plot and the corresponding samples were collected. After two days the concentrations of *cis* and *trans* 1,3-dichloropropene in the interior of the clods were about 0.70 times those at the outside. After 7 days the concentrations inside were higher, and amounted to 1.20 times those in the outside parts. From these measurements alone it is not clear whether the doses obtained for the interior of the clods are lower than those for the outside.

The effect of clods in the plough layer was studied in more detail by carrying out computations for simplified situations. Because structure problems often occur with loamy soils, the situation at the trial site at Bant was taken as a starting point. The clods were assumed to have diameters of 8 cm and to be situated at various depths in the plough layer. In Case 23 they were placed immediately under the soil surface in a sequence with equal volumes of looser soil. The repeating geometrical unit is represented in Fig. 25. The physical properties of the soil were derived from the experimental results for the relevant plots and are given in Table 9. The coefficient D_p for diffusion in the looser soil is about 10 times that for diffusion in the clods.

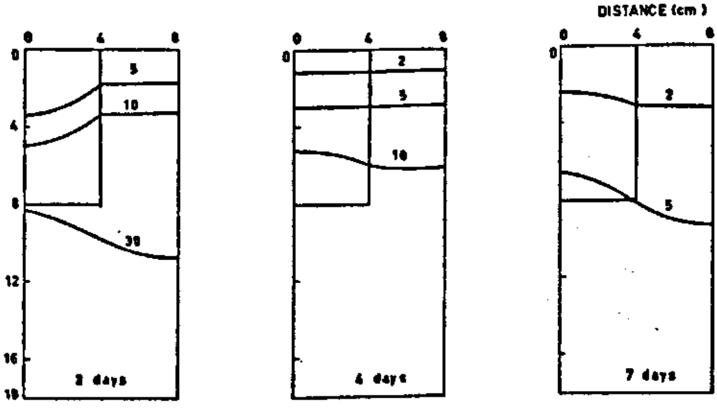


Fig. 25 Iso-concentration lines for *trans*-1,3-dichloropropene in the water phase 2, 4, and 7 days after application to a sandy loam. Simulated Case 23: clods just underneath the soil surface. Concentrations in µg/cm³.

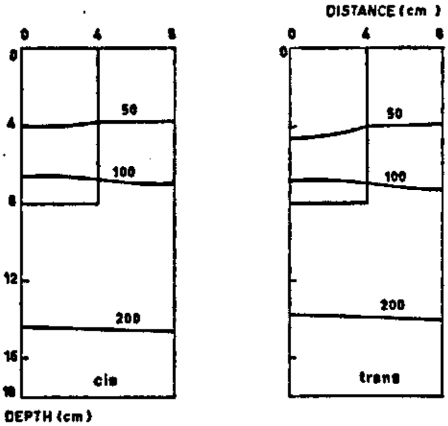


Fig. 26. Iso-dose lines for *cis* and *trans* 1,3-dichloropropene in a sandy loam plough layer with clods just underneath the soil surface. Simulation, Case 23. Doses in (μg/cm³) × day for the water phase.

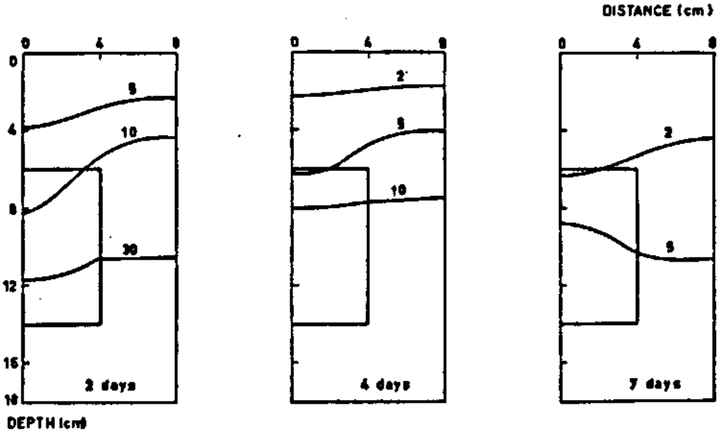


Fig. 27 Iso-concentration lines for *trans*-1,3-dichloropropene in the water phase 2,4 and 7 days after application to a sandy loam. Simulated Case 24: clods with centre at 10 cm depth. Concentrations in μg/cm³.

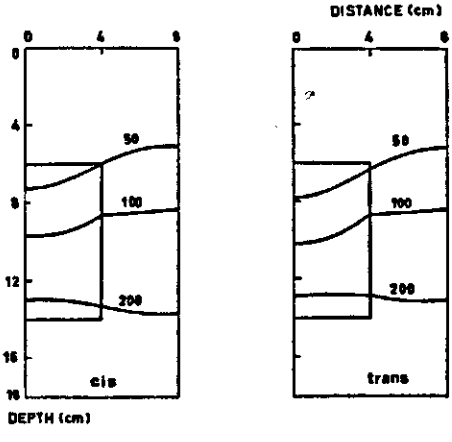


Fig. 28. Iso-dose lines for *cis* and *trans* 1,3-dichloropropene in Case 24: sandy-loam plough layer with clods situated with their centre at a depth of 10 cm. Doses in (μg/cm³) × day for the water phase.

Concentrations of *trans*-1,3-dichloropropene computed for three time intervals after application of the fumigant are given in Fig. 25. The *cis* isomer shows the same behaviour but the diffusion rate is higher. During the first days the concentrations within the clods were lower. The penetration from below was favoured by the high concentration gradient around the lower side of the clod. Furthermore there was a distinct penetration of the clods from the looser soil between the clods. After 4 days the iso-concentration lines were nearly horizontal. From the lines for 7 days it follows that the concentrations in the clods were even higher because the fumigant disappeared from the looser soil more quickly. The total disappearance rate at the soil surface was slowed down by the clods.

The values of the concentration-time integral were computed for *cis* and *trans* 1,3-dichloropropene and are given in Fig. 26. It is found that the iso-dose lines are nearly horizontal. The presence of the clods in this simulated situation was not unfavourable and the slowing down of the disappearance rate was even favourable. However, a serious disadvantage of clods at the soil surface is that they interfere with the necessary finishing-off after fumigant application. See Section 5.3.5.

Next the effect of clods at a greater depth is considered. The centres were placed at 10 cm depth and the cross-section was again 8 cm. Iso-concentration lines for *trans*-1,3-dichloropropene in Case 24 are given in Fig. 27. At the depth of the clods the same pattern is found as with the shallow clods in Case 23. Besides, there appeared to be a sort of shade-effect: in the soil above the clods the concentration was always lower. This can be seen from the doses, which are given for *cis* and *trans* 1,3-dichloropropene in Fig. 28. Furthermore the iso-dose lines were situated about 2 cm deeper in the soil than the corresponding lines in Case 23. The supply of fumigant to the upper soil centimeters was slowed down by the clods and as a result more fumigant was decomposed before this critical region was reached. Further the disappearance rate from the upper centimeters was quicker with this loose soil than with denser soil at this depth. It must be remembered that this is a two-dimensional model for a geometrically three-dimensional system. Thus, in practice the shade-effect shown in Fig. 28 will be smaller.

In weather conditions that are suitable for soil fumigation, nearly equivalent concentration-time products are obtained throughout clods of the size considered here or smaller. An exception has to be made for wet soils because then the clods will be poorly penetrated (Section 5.4.4). As has been shown in Section 5.3.3 the rototilling of the soil is unfavourable, because the soil will be very loose and the fumigant diffusion rate very high. The result is that values for the concentration-time integral are comparatively low, especially for dryer soils. It will thus be necessary to avoid large clods, without making the soil too loose.

The particular situation considered here was one with a high decomposition rate for *cis* and *trans* 1,3-dichloropropene. For soils and conditions with low decomposition rates the slowing-down effect of the clods will have less serious consequences. The permissable clod size will then be slightly greater than that for the situation considered in this section.

5.3.5 Condition of soil surface

After fumigant application much work is done to finish-off the soil surface. The injection equipment is normally followed by implements such as crumblers, harrows, drags and rollers. The effect of these treatments may be judged visually. The question is then how to interpret the observations with respect to fumigation effectivity. Irregularities in the soil surface, like cracks and protruding clods, have to be considered. Another point is whether compressing the top centimetres of the soil is better than only levelling the soil. Heavy rain may change the soil surface. In this section, the importance of the soil surface condition for the dose pattern is discussed, using simplified models of situations that occur in practice.

For a loamy soil the effect of cracks in the soil surface was investigated. Case 23, in which there was a sequence of clods and loose soil at the soil surface, was taken as the starting situation. Clods are often accompanied by cracks because rolling is not effective with a cloddy surface. The geometrical unit for Case 25 includes cracks, which are assumed to be 2 cm deep, and is given in Fig. 29A. In these cracks quick diffusion will take place, whilst removal is speeded up by air flow. It is thus a good approximation to maintain the concentration within the crack at zero. In Fig. 29A the iso-dose lines computed for *cis*-1,3-dichloropropene in this situation are given. For comparison the lines, that would have been obtained without cracks are shown. The cracks clearly caused a lower position of all iso-dose lines. Consequently the nematode mortality will be lower. When cracks occur in practice they are often deeper than 2 cm. Cracks thus reduce fumigation effectivity considerably.

A related problem is the protusion of clods from the soil surface. The doses computed for *cis*-1,3-dichloropropene in Case 26, in which the clods protrude 4 cm, are shown in Fig. 29B. It can be seen that in this situation more top soil was badly fumigated than with a well-finished soil surface. The doses in the part of the clod above the soil surface were much too low for a good mortality percentage, although there

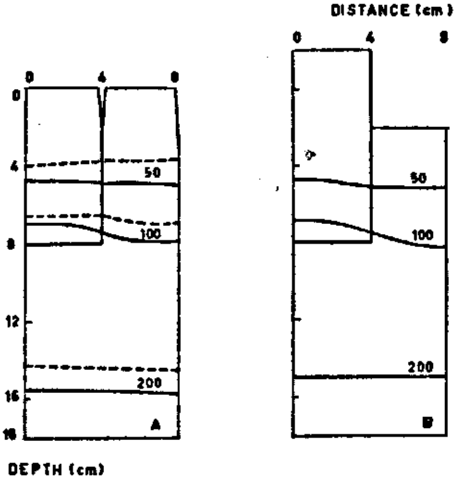


Fig. 29. Iso-dose lines for *cis*-1,3-dichloropropene in a sandy loam with irregular surface. Doses in (μg/cm^3) × day.
A = with cracks of 2 cm depth (Case 25). B = with clods protruding 4 cm from the looser soil level (Case 26)
– – – – = iso-dose lines obtained in absence of cracks (Case 23)

were no cracks between clods and the surrounding soil. However, cracks usually occur with clods in the soil surface. The clods should thus be broken up in the upper centimeters of the soil before further finishing-off.

In Section 5.2.1 the rolling of the soil surface seemed better than the just levelling. This difference is now analysed in more detail with models. The starting point is Case 3, in which the humic sandy soil was only levelled with a drag after fumigant application with a plough injector. The effect of rainfall was not considered here. The doses for *cis*-1,3-dichloropropene in Case 27 are given in Fig. 30. In the next situation, Case 28, the soil surface was firmly rolled, so that a top layer of 4.8 cm became denser. The physical properties for this situation are given in Table 9. The computed doses are also represented in Fig. 30. Rolling affects the doses in the soil favourably. The top layer in which the doses are too low, was about 2 cm smaller than with levelling. Because of this, the extra mortality percentage obtained by firmly rolling can amount to more than 10% of the total nematode population.

The finishing-off by rolling is not always successful. Even with a crumbled top layer, cracks some centimeters deep may be present in the rolled surface at regular intervals. A situation is now simulated that may be typical for humic sandy soil

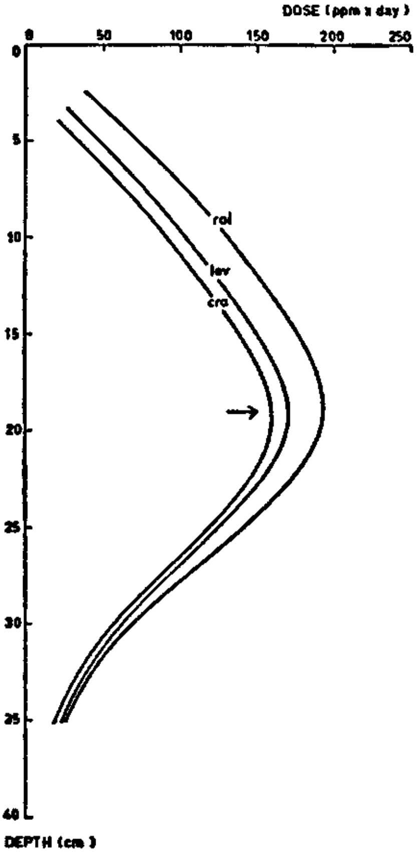


Fig. 30. Doses for *cis*-1,3-dichloropropene obtained with fumigation of a humic sandy soil.
lev = soil surface only levelled (Case 27)
rol = soil surface rolled (Case 28)
cra = cracks in the rolled soil surface (Case 29)

(Case 29). Cracks are taken with a depth of 3.2 cm and at intervals of 6.4 cm. The doses obtained for *cis*-1,3-dichloropropene in this Case are represented in Fig. 30. The favourable effect of rolling was completely offset by the presence of the cracks. There was a thick upper soil layer that is badly fumigated. The difference in position of the iso-dose lines was nearly equal to the depth of the cracks. Therefore this problem deserves attention. Rolling systems that do not produce cracks should be tested.

To interpret nematode mortalities from field trials, conditions have to be studied for at least some weeks after the application of the fumigant. Often there will be rain when there are still active concentrations in the soil. It is interesting therefore to study the effect of rainfall on the values of the doses, to see how important is the rainfall and what effect it has on the dose pattern. Therefore the redistribution of the water in soil was simplified to a stepwise process. For the reference situation the first nine days of Case 1 are taken. A rather dry humic sandy soil was fumigated with a plough injector (Case 30). The doses obtained for *cis*-1,3-dichloropropene are given in Fig. 31.

In the new Case 31 it is assumed that the moisture condition was constant only for the first three days. In this period there was a considerable spread of the fumigant and some had disappeared at the soil surface. In a second period of three days, the

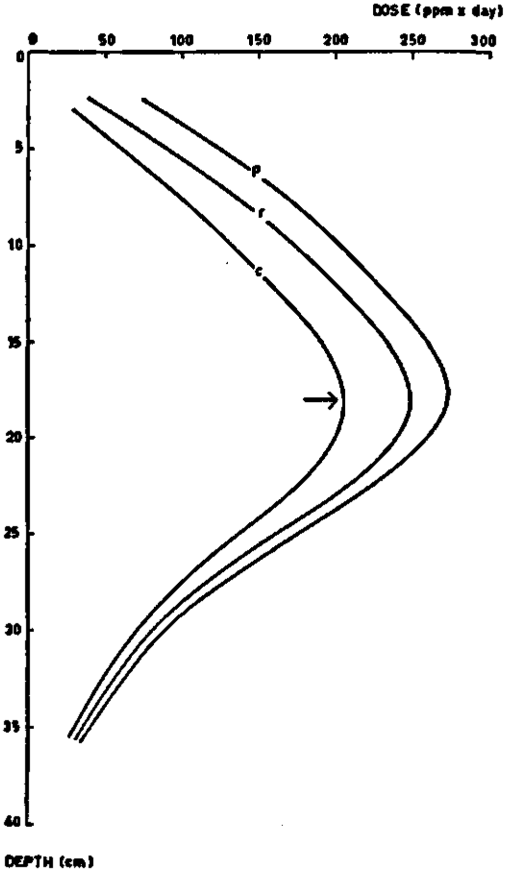


Fig. 31. Doses obtained for *cis*-1,3-dichloropropene in a humic sandy soil.
c = constant moisture content, Case 30
r = increase in moisture content by 15 mm of rainfall, Case 31
p = increase in moisture content and puddling through 15 mm of rainfall, Case 32

water from a shower of 15 mm was in the layer of 0–6 cm. The relevant soil properties are given in Table 9. The new value of D_p is inferred from the literature data in Section 2.2. In the third period lasting from 6 days onwards, the water was evenly distributed in the layer of 0–18 cm. The doses obtained for *cis*-1,3-dichloropropene in this Case 31 are also given in Fig. 31. It can be seen that the doses were considerably higher than those in the dryer Case 30. A higher nematode mortality will result because the fumigation of the upper soil centimeters was better. In another situation, indicated by Case 32, the circumstances are the same as in Case 31, but a puddling effect of the rain at the soil surface is included. Such an effect may be expected with an intensive shower on a well-rolled soil surface. The result is an extra reduction of the diffusion coefficient D_p in the upper centimetres (Fig. 12). The relevant physical data are given in Table 9. The doses computed for *cis*-1,3-dichloropropene are represented in Fig. 31 and show that an increase in the doses was obtained. The puddling of the soil surface and the considered increase in moisture content influenced the dose to a similar extent. Under the conditions considered here, high nematode mortalities (sometimes in excess of 90%) are indeed found in practice. With fumigation of greenhouse soils, a powerful water jet is often used to obtain the desired slowing-down of the diffusion near the soil surface.

5.4 Weather conditions

During the periods in which fumigants are applied to field soils, the weather is very changeable. Some fumigations can be carried out in late summer after harvest of early crops. The majority of fumigations are carried out around September. However, some crops like sugar-beet are harvested throughout the autumn and if possible the farmers would like to fumigate afterwards. There can be a wide range of soil temperatures and moisture contents in these periods. The question is under what conditions is fumigation effective. There has been controversy about the relative importance of temperature and soil moisture content. Further procedures are required to measure quickly any changes in soil conditions related to weather. Only with an accurate warning system can full advantage be taken of the most favourable periods. This is particularly urgent as the fumigation period mainly coincides with the harvesting period. As weather conditions may vary from year to year it is not a good idea to set a deadline for fumigation. The most important weather factor should be found as a first step in establishing a good system of recommendations.

5.4.1 Fumigation at different temperatures

The first fumigation at the trial field at Oranje was carried out on 3 September 1969. The layout was similar to that for the fumigation of this field on 15 October, discussed in Section 5.2.1. From the characteristics of the soil layers, given in Table 11, it follows that the moisture condition during the first trial was similar to that for the October fumigation (Table 7). However, an important difference was the average soil

Table 11. Properties of soil layers and diffusion and adsorption characteristics of *cis* and *trans* 1,3-dichloropropene. Fumigation of the field near Oranje on 3 September 1969 with plough injector plus roller (Case 33), plough injector plus drag (Case 34), blade injector (Case 35) and shank injector (Case 36). Computation of the doses at 17 °C (Case 33), 12 °C (Case 37) and 7 °C (Case 38). Effect of a limited increase in moisture content (Case 39). Loose and dense parts in a plough layer under wet (Case 40) and moist (Case 41) conditions.

Case	Layer or part	Depth (cm)	ρ_b (g/cm^3)	*omc* (g/g)	ε_w (cm^3/cm^3)	ε_g (cm^3/cm^3)	D_p (cm^3/(cm · s); × 100)		Φ (cm^3/cm^3)	
							estimation range	approximated value	*cis*	*trans*
33	a	0–18	1.22	0.055	0.16	0.36	1.00–1.70	1.36	23	40
	b	18–30	1.42	0.049	0.20	0.25	0.32–0.71	0.37	25	42
	c	30–42	1.40	0.037	0.17	0.29	0.44–0.83	0.75	19	32
34	a	0–19	1.18	0.055	0.15	0.39	1.40–2.10	1.80	22	38
	b	19–30	1.42	0.049	0.20	0.25	0.32–0.71	0.37	25	42
	c	30–42	1.40	0.037	0.17	0.29	0.44–0.83	0.75	19	32
35	a	0– 7.5	1.19	0.055	0.14	0.39	1.40–2.10	1.80	22	38
	b	7.5–15	1.32	0.055	0.17	0.31	0.60–1.20	0.90	25	43
	c	15–30	1.44	0.050	0.20	0.24	0.24–0.67	0.25	25	43
	d	30–42	1.40	0.037	0.17	0.29	0.44–0.83	0.75	19	32
36	a	0– 6.5	1.25	0.055	0.14	0.37	1.20–1.90	1.80	23	40
	b	6.5–13	1.42	0.055	0.20	0.26	0.32–0.90	1.00	25	45
	c	13–30	1.44	0.050	0.20	0.23	0.20–0.63	0.25	25	43
	d	30–42	1.40	0.037	0.17	0.29	0.44–0.83	0.75	19	32
37	a	0–18	1.22	0.055	0.16	0.36		1.32	31	53
	b	18–30	1.42	0.049	0.20	0.25		0.36	33	57
	c	30–42	1.40	0.037	0.17	0.29		0.73	25	43
38	a	0–18	1.22	0.055	0.16	0.36		1.27	42	73
	b	18–30	1.42	0.049	0.20	0.25		0.35	44	78
	c	30–42	1.40	0.037	0.17	0.29		0.70	34	60
39	a	0–18	1.22	0.055	0.25	0.27		0.81	33	57
	b	18–30	1.42	0.049	0.26	0.19		0.19	34	59
	c	30–42	1.40	0.037	0.24	0.22		0.37	27	47
40	loose	0–14	0.77	0.19	0.40	0.26		1.04	105	175
	dense	0–16	0.94	0.19	0.58	0.01		0.000165	$\psi = 3.0$	$\psi = 3.2$
41	loose	0–14	0.77	0.19	0.30	0.37		1.48	100	168
	dense	0–16	0.94	0.19	0.38	0.21		0.30	123	206

temperature of 17 °C for the September trial. Therefore, the effect of temperature on the concentration-time relation could be examined. The four treatments involved were: plough injection with roller (Case 33); plough injection with drag (Case 34); subsurface-blade injection (Case 35) and shank injection (Case 36).

The concentrations were determined 3 and 10 days after fumigant application. The results of the different treatments are given in Table 12. The differences were similar to those found for the trials dealt with in Section 5.2.1. It is favourable to roll the soil surface firmly after plough injection. There is also a gradual penetration into the denser soil between the injection tracks after shank injection. Three days after fumigation at 17 °C the concentrations were lower than at the corresponding time after fumigation at 12 °C. An exception is blade injection because a lower rate was applied during the October fumigation (Section 5.2.1). There was hardly any rainfall in the first weeks after fumigation on 3 September; the diffusion rates remained high and after 10 days the concentrations had fallen to rather low values.

It is interesting to isolate the effect of temperature from the influence of other fac-

Table 12. Concentrations of *cis* and *trans* 1,3-dichloropropene in the water phase at different depths in soil after fumigation of field near Oranje on 3 September 1969. Time in days, depth in cm, and concentrations in μg/cm³. Case 33 = plough injector + roller, Case 34 = plough injector + drag, Case 35 = blade injector, and Case 36 = shank injector.

Time	Compound	Case 33		Case 34		Case 35		Case 36		
		Depth	C_w	Depth	C_w	Depth	C_w	Depth	C_w (tracks[1])	C_w (between[2])
3	*cis*-1,3 D	4	5.3	4	3.4	4	4.3	5	4.9	4.4
		11	15	12	12	10	14	13	16	13
		18	25	19	20	16	21	21	7.3	4.0
		28	8.2	29	7.5	25	7.5	29	1.4	0.6
		41	0.5	41	0.3	37	0.3	41	0.0	0.0
	trans-1,3 D	4	5.4	4	4.2	4	5.9	5	7.5	6.5
		11	15	12	14	10	17	13	22	16
		18	25	19	21	16	24	21	5.8	3.9
		28	5.3	29	5.5	25	4.2	29	0.3	0.1
		41	0.2	41	0.2	37	0.2	41	0.0	0.0
10	*cis*-1,3 D	4	0.8	4	0.5	4	0.5	5	0.7	0.5
		11	3.0	12	1.7	10	1.7	13	3.3	2.8
		18	6.2	19	3.5	16	3.7	19	4.2	3.0
		29	3.6	29	3.8	25	4.3	29	1.6	1.2
		45	0.3	45	0.4	45	0.1	45	0.0	0.0
	trans-1,3 D	4	1.3	4	1.0	4	1.2	5	1.3	1.1
		11	4.5	12	3.1	10	3.5	13	5.5	4.8
		18	8.9	19	5.9	16	7.2	19	5.3	4.6
		29	4.5	29	4.4	25	4.7	29	1.7	1.1
		45	0.3	45	0.4	45	0.0	45	0.0	0.0

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1. Sampled on tracks.
2. Sampled midway between tracks.

tors on the concentration-time relation. For that purpose a series of computations were carried out starting from the situation in Case 33: fumigation at 17 °C by plough injection with finishing-off by rolling. The only primary factor varied was temperature: 12 °C (Case 37) and 7 °C (Case 38) were selected for the series. The relations between the values of the basic data and temperature were discussed in sections 2.1 and 2.2. The relevant properties of the soil layers and the diffusion and adsorption characteristics for the isomers of 1,3-dichloropropene are given in Table 11.

The doses of *cis* and *trans* 1,3-dichloropropene obtained for the three temperatures are represented in Fig. 32. It follows that the doses were highest at the lowest temperature. At the higher temperatures there was a comparatively high concentration in the gas phase (Section 2.1) so that diffusion took place quickly and values of the concentration-time integral were low. Also with decreasing temperature hardly any fumigant is withdrawn from the water phase by the adsorbing phase (Section 2.1). From Fig. 32 it follows that differences in mortality will be caused by differences in

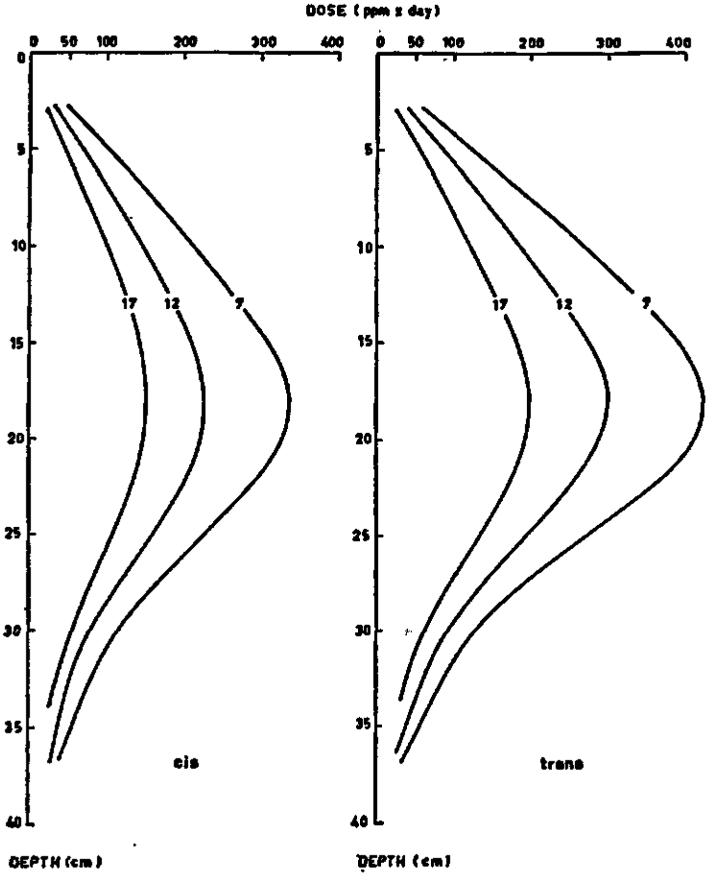

Fig. 32 Doses of *cis* and *trans* 1,3-dichloropropene computed for the fumigation of a humic sandy soil at 17°C (Case 33), 12°C (Case 37), and 7°C (Case 38).

the thickness of the insufficiently fumigated layer underneath the soil surface.

Together rather dry soil and a high soil temperature reduce the nematicidal effectivity of a fumigant. This confirms the results of earlier investigations. However, still under discussion was the lowest soil temperature suitable for soil fumigation. From the literature data discussed in Section 2.4 it follows that the nematicidal activity of 1,3-dichloropropene is probably not strongly influenced by the temperatures in the autumn range. The doses at 7 °C were higher than at the other temperatures so that nematode mortality will be good. In the past it was difficult to interpret results from trial fields because low autumn temperatures were often associated with high soil moisture contents. The results given in this section make it clear that failure with dichloropropene can not be attributed to the effect of low temperatures.

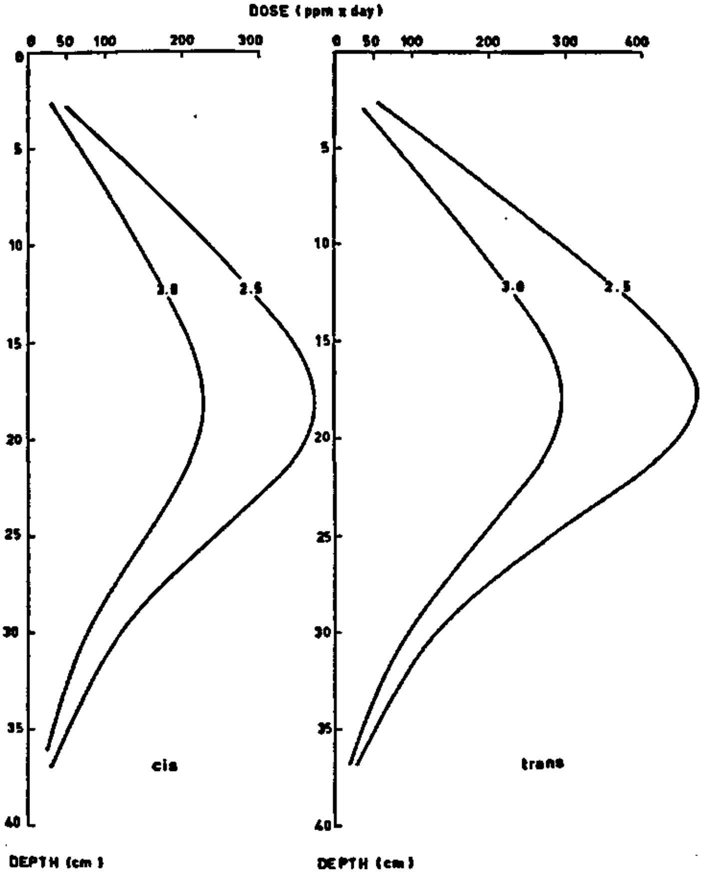

Fig. 33. Effect of a limited increase of the soil moisture content on the doses for *cis* and *trans* 1,3-dichloropropene. Moisture contents approximately corresponding with pF=3.0 (Case 37), and with pF=2.5 (Case 39)

5.4.2 Influence of soil moisture

Soil moisture content may vary considerably in the autumn when soils are fumigated. To study how much higher the doses obtained for the trial sites in the autumn of 1969 (cf. sections 5.2.1, 5.3.1 and 5.4.1) would have been if the moisture content was somewhat higher, this content was varied in the computations. Case 37 was taken as the reference situation. The moisture content corresponded approximately with pF = 3 (de Vries & Dechering, 1960). For the computations on Case 39 the moisture content was increased to a content at about pF = 2.5. The physical characteristics for the layers in Case 39 are given in Table 11. The new values of D_p were derived from the basic data discussed in Section 2.2.

The doses for *cis* and *trans* 1,3-dichloropropene in cases 37 and 39 are represented in Fig. 33. For the situation with a higher moisture content the doses were considerably higher. This favourable effect of the higher moisture content, in the range in which a well-distributed system of gas-filled pores is present, is the result of the slowing-down of the diffusion rate. The values of the concentration-time integral then become higher. From the values of the fumigant capacity factor Φ given in Table 11, it follows that at higher moisture contents only a small additional amount of fumigant is sorbed from the gas phase. Therefore the lower diffusion rate results mainly from the lower value of D_p, which is connected with the smaller gas volume available for diffusion and the increasing geometrical complexity of the pore system.

Fig. 33 indicates that moisture content is one of the most important factors for soil fumigation. A presupposition in the computations was that there is a well distributed and continuous system of gas-filled pores in the soil. Such a system is not present when moisture contents are very high so that the situation then drastically changes as is described in Sections 5.4.3 and 5.4.4.

5.4.3 Soil fumigation at high moisture contents

If there is no objection to fumigating wet soils then fumigations could be carried out late in autumn, so that the work is distributed more evenly over the season. However, most late fumigations have resulted in low nematode mortalities. To find out possible causes for this, fumigation of a peaty sand on peat profile was studied under wet conditions. The field was situated near Borgercompagnie and was fumigated on 9 November 1970. The profile consisted of a 20 cm thick top layer of peaty sand (19% w/w organic matter) with a peat layer underneath. The moisture content during fumigation was high ($\varepsilon_w = 0.48$) and even slightly increased in the weeks following the application as a result of rainfall (2 mm per day on the average). The high moisture content was also due to the low water permeability of the peat layer. A rate of 265 litres of dichloropropene mixture per hectare was applied with a plough injector. The injection depth was 16 cm and the soil surface was fairly well finished-off with a roller. The samples were taken from five plots at the trial site and from six depths. Per plot soil samples were taken from 5 places and the soil was collected per depth. The three sampling times were 4, 11 and 23 days after application.

The five concentrations obtained for each depth were found to vary greatly for all three time intervals. The standard deviations ranged up to 80% of the average values and near the injection depth the deviations were even higher. This implies that the distribution of the fumigant through the soil was very irregular. The high concentrations near the injection depth suggest a slow release of the fumigant and low concentrations at other depths indicate that penetration in parts of the soil was poor. From the measured physical characteristics of the soil it follows that the volume fraction of gas-filled pores, ε_g, ranged from 0.03 at the bottom of the peaty sand layer to 0.14 near the soil surface. Thus a large part of the soil had values of ε_g smaller than 0.10. From the results on the relation between D_p/D_a and ε_g discussed in Section 2.2.2 it follows that many pores were probably completely blocked for gas and vapour diffusion. Therefore in large sections of the soil profile that possibly had high nematode densities, doses were much too low.

To give a rough impression of the concentration patterns in the soil profile at the three intervals of time, the averages of the measured concentrations of *cis* and *trans* 1,3-dichloropropene are given in Fig. 34. The picture near the injection depth was obscure, as there were very high concentrations in some samples even 23 days after fumigant application. Because of slow spreading, the concentrations C_w in the layer

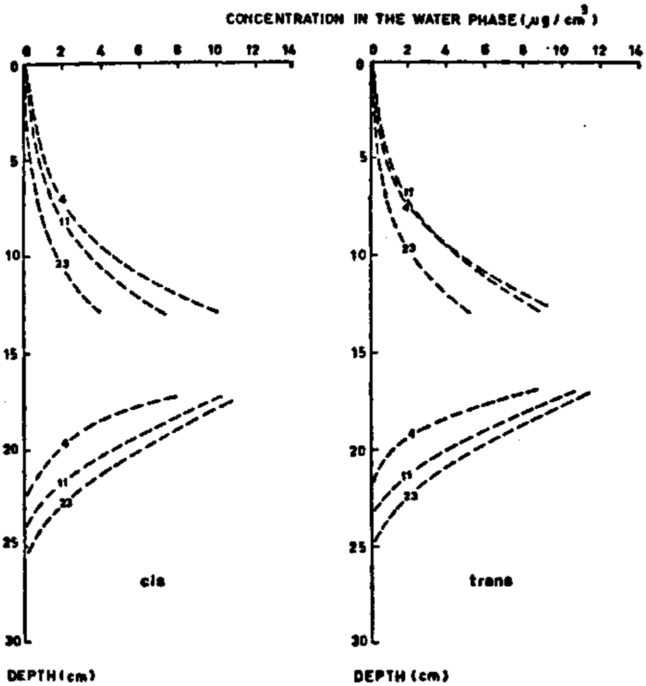

Fig. 34. Outline of the relation between the averages of the concentrations of *cis* and *trans* 1,3-dichloropropene and depth after fumigation of a peaty sand on peat soil under wet conditions. Time intervals 4, 11, and 23 days after application.

of 0 to 8 cm hardly rose above 2 μg/cm^3. Thus to depths of 10 cm doses were on the average insufficient for a good nematode mortality. The small concentration gradients at shallow depths indicate that the fumigant only disappeared slowly at the soil surface. The extremely slow penetration into the peat layer is in agreement with the slow diffusion in cases 2 and 16 for the same type of layer under dryer conditions. At 30 cm depth concentrations were not measurable by the standard method ($C_w <$ 0.01 μg/cm^3).

The question might be asked whether the situation would improve when the soil becomes dryer. Soil normally dries from above, so that there will be a faster upward diffusion through the dryer soil, while the upward diffusion through the lower wetter part of the soil is slow. The improved spreading in the dryer layer will occur at very low concentrations so that nematode mortality will hardly increase. Usually peaty sand soils are ploughed in winter and in the case considered here this had been done a month after application. The great amount of fumigant then still present near the injection depth will be largely displaced to shallower depths and escape through the rough soil surface. Much of the fumigant applied is thus ineffective for soil fumigation.

The two main causes of failure with soil fumigation under wet conditions are the slow release of the fumigant and its uneven distribution throughout the soil. On account of such a concentration pattern, nematode mortalities will be very low. This was confirmed by mortality percentages obtained for trial fields with nearly the same soil type and under similar conditions.

5.4.4 Further analysis of fumigation under wet conditions

To carry out computations on diffusion of 1,3-dichloropropene in wet soil, the procedures for dryer soil cannot be used. From the concentration measurements for the trial site at Borgercompagnie it follows that the presuppositions, dealing with a quick release of the fumigant from the injection position and with penetration into all soil parts, do not apply. In view of the high soil moisture content it is probable that, shortly after application, a great part of the fumigant was surrounded by soil parts and water. Then the initial transport process is diffusion through the water phase. This is a slow process compared with diffusion through the gas phase. In the ploughed layer there were denser soil parts that were not broken up during application with the plough injector. The measurements of bulk density and moisture content indicated that in these soil portions the pore system was nearly completely filled with water. Another part of the ploughed layer was disturbed and loosened, and there a gas-filled pore system was available for fumigant vapour diffusion.

For the computations the situation was taken as outlined in Fig. 35. At first the fumigant diffused through the water phase in a 2 cm thick soil layer. In the layer 0–14 cm, a horizontal sequence of 8 cm wide bands of denser and looser soil was assumed. The repeating geometrical unit bounded by reflection planes was then the one given in Fig. 35. The soil physical characteristics for this simulated fumigation situation, indicated as Case 40, are given in Table 11. The temperature was assumed to be 6 °C.

It is interesting to compare the coefficients for the diffusion of 1,3-dichloropropene in the looser and denser soil portions. The coefficient D_a for 1,3-dichloropropene in air at 6 °C was 7.4×10^{-2} cm^2/s (Fig. 6). For the gas-filled pore system in the looser soil, D_p can be estimated to be 1.04×10^{-2} cm^3/(cm·s). With a fumigant capacity factor $\Phi = 105$ the effective diffusion coefficient $D_m = D_p/\Phi = 0.985 \times 10^{-4}$ cm^2/s. The coefficient D_w for the diffusion of 1,3-dichloropropene in water at 6 °C was about 5.7×10^{-6} cm^2/s. For the diffusion in the water-filled pore system in the denser soil, $D_{pw} = 1.65 \times 10^{-6}$ cm^3/(cm·s). Another type of fumigant capacity factor was involved in the diffusion in the water phase: $\psi = \varepsilon_w + \rho_b \cdot K_{s/w}$, in which $K_{s/w} = K_{s/g}/K_{w/g}$. The value of ψ for *cis*-1,3-dichloropropene in the denser soil was 3.0, which was considerably lower than the value of Φ in the looser soil portions. The effective diffusion coefficient for the denser portions was: $D_m = D_{pw}/\psi = 0.55 \times 10^{-6}$ cm^2/s. The coefficient D_m for the diffusion of *cis*-1,3-dichloropropene in the looser portions (diffusion mainly in the gas phase) was thus about 180 times the corresponding coefficient for the dense portions (diffusion in the water phase). For *trans*-1,3-dichloropropene the ratio was about 115 under these conditions.

Iso-concentration lines computed for *cis*-1,3-dichloropropene at three time intervals after fumigant application are represented in Fig. 35. For the *trans* isomer the same general picture was obtained. The fumigant was gradually released from the injection position. There was a comparatively quick diffusion through the looser soil portions but no high concentrations built up. The diffusion in these portions took place at low concentration levels. In the denser soil portions the concentrations near the injection position were high but penetration was very poor. The penetration of the fumigant from the looser soil into the denser parts was also extremely slow, because the concentration gradient available was too low to compensate for the high diffusion resistance. From the concentration patterns in Fig. 35 it is not surprising that, when concentrations are determined in similar situations, the results vary greatly. As in the situation for which the measured concentrations are given in Fig. 34 there was a long period

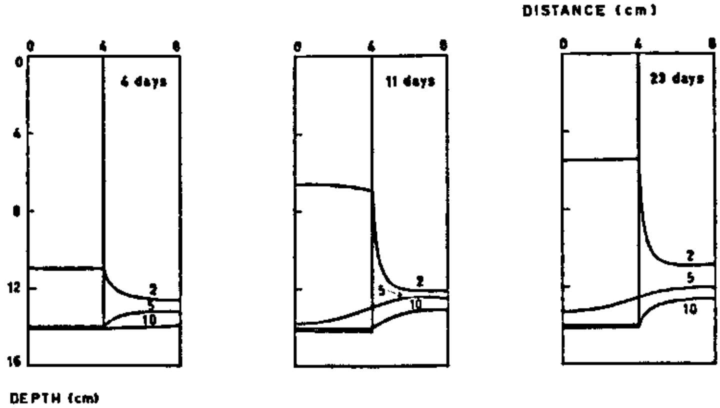

Fig. 35. Iso-concentration lines for *cis*-1,3-dichloropropene 4, 11, and 23 days after application. Simulation of a fumigation under wet conditions. Case 40. Concentrations in the water phase in µg/cm^3.

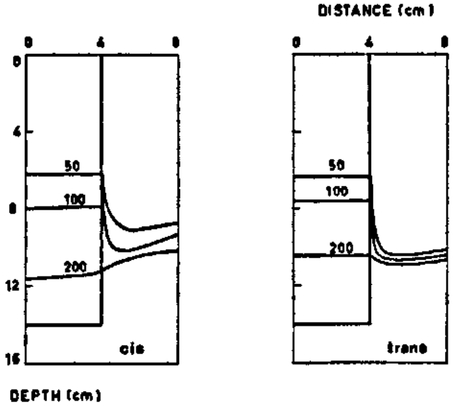

Fig. 36. Doses obtained for *cis* and *trans* 1,3-dichloropropene with a fumigation under wet conditions. Case 40. Doses in ppm × day.

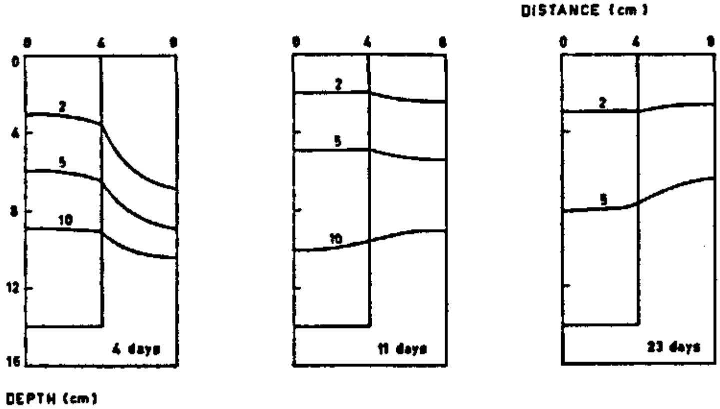

Fig. 37. Iso-concentration lines for *trans*-1,3-dichloropropene 4, 11, and 23 days after application. Simulation of fumigation of a plough layer with dense and loose parts and with a soil moisture content approximately corresponding with pF=2.5. Case 41. Concentrations in the water phase in μg/cm³.

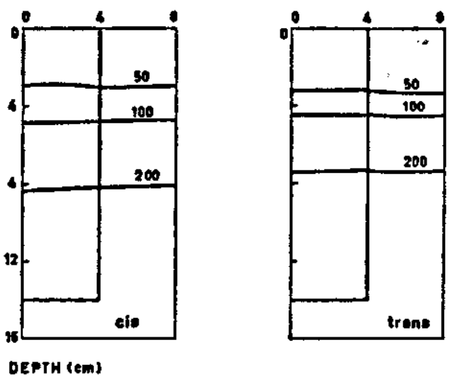

Fig. 38. Iso-dose lines for *cis* and *trans* 1,3-dichloropropene obtained for a peaty-sand plough layer (Case 41). Soil moisture contents approximately correspond with pF=2.5. Doses in ppm × day.

with high concentrations near the injection position and low concentrations at some distance from it.

The doses achieved for *cis* and *trans* 1,3-dichloropropene in the situation simulated here are given in Fig. 36. The looser soil portions were badly fumigated: there was a thick top fraction with a low nematode mortality. The fumigation of the denser soil parts was even worse.

To investigate the real cause of the difficulties, simulation computations were carried out for the same geometrical situation as that outlined in Fig. 35 and for the same temperature, but the soil moisture contents were lower. Values were taken that correspond for these soils with about pF = 2.5 (de Vries & Dechering, 1960). The soil physical properties for this Case 41 are given in Table 11. A very important difference with the wet variant Case 40 was that in the denser soil parts a gas phase is available for fumigant vapour diffusion. The D_p value for the denser parts was about 1/5 of that for the looser parts. Therefore in Case 41 there were no extreme differences in D_p values.

Concentrations of *trans*-1,3-dichloropropene at three time intervals after the application of the fumigant are given in Fig. 37. For the *cis* isomer the diffusion rate was greater, but a similar pattern of iso-concentration lines was obtained. In an initial period the concentrations in the denser soil portions were lower, but there was a distinct gradual penetration of the fumigant. In a second period the concentrations at the various depths in the looser and denser soil were nearly equal. In a last period the higher disappearance rate of the fumigant from the looser soil became predominant so that the concentrations in the denser soil were highest. Thus there was a reversal in the concentration gradient between the looser and denser soil portions (cf. Section 5.3.4).

The doses computed for *cis* and *trans* 1,3-dichloropropene are given in Fig. 38. The iso-dose lines are nearly horizontal. This is connected with the phenomenon that the period with great concentration differences between the looser and denser soil portions was comparatively short, whereas the period with smaller differences of opposite nature was longer. It can be seen from the position of the 50 and 100 ppm × day lines that this situation is much more favourable than the wet one (cf. Fig. 36). The conclusion is that the high moisture content caused the difficulties. At lower soil moisture contents the presence of denser soil parts was in itself not a serious impediment to reasonable effectivity. Indirectly the presence of looser and denser soil parts may give rise to problems of the type discussed in the sections 5.3.4 and 5.3.5.

6 Prevention of undesirable side-effects

6.1 Nature of side-effects

With all soil fumigants, including 1,3-dichloropropene, a waiting period has to be observed after application. As 1,3-dichloropropene has fytocidal and bactericidal properties besides nematicidal properties a waiting period of about a month is necessary. However, undesirable side-effects like phytotoxicity may even occur after the recommended waiting period. Sometimes crops have been damaged in spring, some months after fumigant application. This does not happen every year or everywhere, so that presumably it can be avoided.

In 1969, Hijink described the damage to oats which is susceptible to dichloropropene residues: growth is stunted and the older leaves and the tops of younger leaves die. In spring 1970 this damage was observed at a number of sites, with both humic sand and peaty sand soils. The sites involved were fumigated under rather wet conditions, late in the autumn of 1969. Soon after there was much rain in the area and during nearly the whole winter the top soil was frozen.

In autumn 1970 several fields of loamy soil were fumigated with dichloropropene mixture and some weeks thereafter winter wheat was sown. In 1971, the winter wheat was found to have ears which were much shorter and in a number of cases a loss in yield was the result.

Off-flavour and abnormal smell of food crops like potatoes and carrots are found when fumigant is still present during growth. Therefore it is not permitted to grow ware potatoes in the year following an autumn fumigation with dichloropropene mixture. Grass grown on soil with fumigant residues should not be fed to dairy cattle. This applies to both fresh and ensiled grass.

In some fields where sugar and fodder beets were grown after fumigation with dichloropropene in the previous autumn, the main root rotted or did not develop and many lateral roots formed. Under dry conditions around June wilting symptoms appeared sooner than normal. The yield, both with respect to amount and quality, was then considerably lower.

The nitrogen effect which accompanies soil fumigation with dichloropropene has been extensively studied. The main aspect is the suppressed activity of nitrifying bacteria for some months. As a result less leaching of nitrogen as nitrate occurs in winter and more nitrogen is available in spring. This additional amount may result in too abundant growth so that, for example, with corn crops the risk of lodging is increased.

The question is what can be done to avoid significant concentrations of fumigant being present in soil during the growth of crops. An important point is the initial concentration. The rate of dichloropropene fumigant usually applied is a minimum and only with careful fumigation under favourable conditions will the rate be effective (cf. Chapter 5). Lowering the rate is thus not advisable. The soil and weather conditions are very important for the concentration-time relation and thus for the duration of the period in which aftereffects may occur. Therefore it is interesting to consider the relative importance of the various environmental factors in more detail with respect to disappearance rates.

6.2 Decrease in concentration by diffusion

With low decomposition rates for a fumigant in soil the disappearance by diffusion will be a deciding factor. Thus again it is important to consider the effect of soil and weather on the diffusion rates. The concentration at the injection depth is normally representative of the highest concentrations in the soil and especially of that in the intensively rooted zone. This concentration is therefore a sensitive measure of the rate of the diffusion process. By taking the concentrations in the water phase, the biological activity of the fumigant can be assessed immediately.

As was discussed in Chapter 5, the organic matter content of the soil, the temperature, and the moisture content affect the diffusion rate. The question is which of these has the greatest influence on the disappearance of residues. Further estimates are needed of how long the waiting periods must be under different conditions. In a series of computations the effect of each factor mentioned was studied separately. The reference situation was as in Case 37: the fumigation of a humic sandy soil under rather dry conditions at 12 °C (cf. Table 11). In Fig. 39 the relation between the concentrations of *cis* and *trans* 1,3-dichloropropene at the injection depth (18 cm) and time is given. Three weeks after fumigant application, the concentration had fallen to such low values, that side effects due to dichloropropene residues were unlikely to occur. This might be a situation in which a waiting period of 21 days is sufficient.

To trace the effect of the organic matter content alone, Case 19 (cf. Table 9) was suitable: the fumigation of a peaty sand soil under rather dry conditions at 12 °C. The concentration-time relations are shown in Fig. 39. As a result of the stronger adsorption the concentration during the first week was lower than that for the humic sandy soil. However for the same reason the diffusion rate was lower so that after the first period the concentrations were higher. The duration of the period, necessary to reach the same low residue level, was about 1.5 times that for the humic sandy soil. In the reference situation, Case 37, the temperature was 12 °C. To check the effect of temperature, computations were carried out for the same situation at 7 °C (Case 38). As is shown in Fig. 39 the diffusion rate was distinctly lower, because of the lower volatility. Therefore a longer waiting period is needed, again about 1.5 times that for the reference situation at 12 °C.

To test the effect of moisture content on the diffusion rate, computations were carried out for Case 42. Details are given in Table 13. This case corresponded with

Table 13. Soil physical characteristics of the soil layers involved in the computations, and diffusion and adsorption characteristics for *cis* and *trans* 1,3-dichloropropene. Decrease in concentration by diffusion in moist soils (pf ≈ 2). Case 42: humic sandy soil. Case 43: peaty sand soil. Contribution of various processes to the disappearance from soil for a rather dry (Case 44) and a wet (Case 45) sandy loam.

Case	Layer or part	Depth (cm)	ρ_b (g/cm^3)	*omc* (g/g)	ε_w (cm^3/cm^3)	ε_g (cm^3/cm^3)	D_p (cm^3/(cm · s); × 100)	Φ (cm^3/cm^3)	
								cis	*trans*
42	a	0–18	1.22	0.055	0.35	0.17	0.39	36	61
	b	18–30	1.42	0.049	0.35	0.10	0.08	37	63
	c	30–42	1.40	0.037	0.31	0.15	0.19	29	49
43	a	0–18	0.90	0.18	0.42	0.19	0.52	106	177
	b	18–30	1.08	0.16	0.44	0.10	0.07	113	188
	c	30–42	1.10	0.12	0.40	0.15	0.19	89	147
44	a	0–18	1.18	0.025	0.19	0.34	1.40	17	
	b	18–30	1.43	0.022	0.25	0.19	0.37	19	
	c	30–42	1.40	0.016	0.22	0.25	0.62	15	
45	a	0–18	1.18	0.025	0.35	0.18	0.39	21	
	b	18–30	1.43	0.022	0.40	0.05	0.04	23	
	c	30–42	1.40	0.016	0.35	0.12	0.15	19	

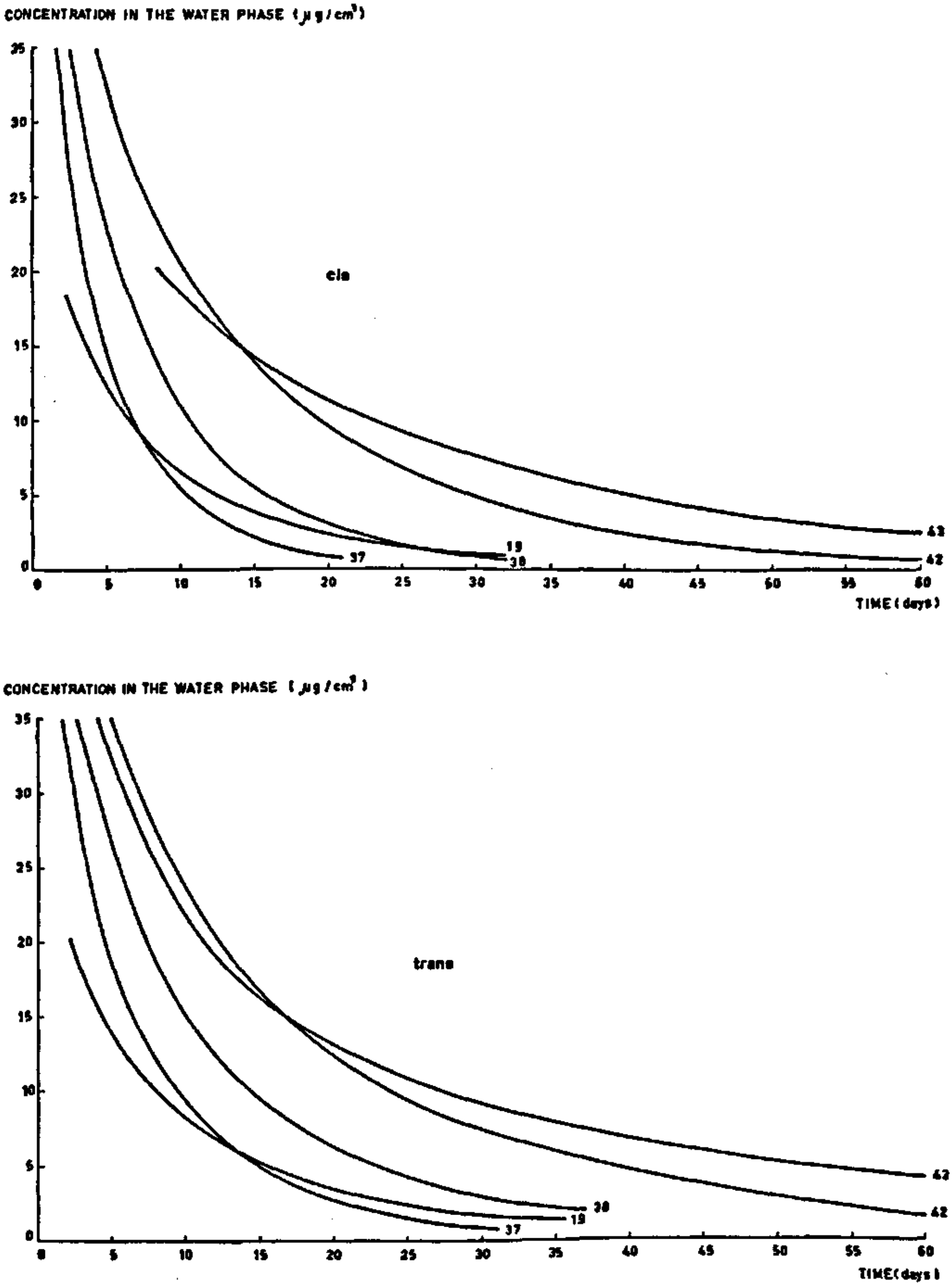

Fig. 39. Concentrations in the water phase of *cis* and *trans* 1,3-dichloropropene at the injection depth (18 cm) in the first months after application. Case 37: humic sandy soil, pF ≈ 3, 12 °C. Case 19: peaty sand soil, pF ≈ 3, 12 °C. Case 38: humic sandy soil, pF ≈ 3, 7 °C. Case 42: humic sandy soil, pF ≈ 2, 12 °C. Case 43: peaty sand soil, pF ≈ 2, 7 °C.

Case 37, except for the moisture content which was higher and corresponded with a pF-value of about 2.0 (de Vries & Dechering, 1960). From Fig. 39 it follows that the diffusion rate was drastically decreased with increasing moisture content. Indications for this strong effect follow directly from the relations between D_p/D_a and ε_g discussed in Section 2.2.2. The moisture content had the most important effect on the duration of the period with side effects. Under these rather wet conditions this period will be about 2.7 times as long as that for the corresponding dryer situation.

Computations were carried out for Case 43 (cf. Table 13) in which a peaty sand soil was fumigated at 7 °C under moisture conditions corresponding with about pF = 2.0. From the concentration-time relation for the injection depth shown in Fig. 39, it follows that, even after 2 months, a large amount of *cis* and *trans* 1,3-dichloropropene was present. Under these conditions it may take 3 months before the risk of aftereffects is sufficiently reduced. Until recently, soils were fumigated at even higher soil moisture contents. It is not surprising that considerable amounts of residue were found in spring. In practice situations may be more complex than outlined here. Peat underneath the plough layer increases the waiting period as then there is strong adsorption and very slow diffusion. On the other hand ploughing reduces the possible residue-level in the plough layer.

To prevent aftereffect problems due to low diffusion rates, soil fumigations should not be carried out under wet conditions. When dichloropropene-sensitive crops are to be grown in spring, it is advisable to fumigate as early as possible.

6.3 Relative contribution of various processes to the disappearance of 1,3-dichloropropene from soil

In numerical computations on the concentration-time relation for a fumigant in soil other computations may be included. The amounts of fumigant that disappear from the root zone by diffusion at the soil surface and by diffusion into the subsoil were calculated. Starting point was flux equation (2). From the finite difference approximation for this equation the following equation is obtained for the amount diffused in the period from t to $t+\Delta t$:

Amount diffused (t to $t+\Delta t$) $= -D_p \cdot \Delta t \cdot \Delta C_g/\Delta x$

This amount is expressed in µg of fumigant per cm^2 soil surface. By summing these amounts over the fumigation period, the total amount is obtained that disappeared by vapour diffusion at the plane considered.

The amount of fumigant decomposed in soil may also be computed. By multiplying the concentrations C_g at time t by the factor $(1-k_r \cdot \Delta t)$ the decomposition is accounted for (cf. Section 3.4). The amount of fumigant per cm^3 soil, that is decomposed in the time interval from t to $t+\Delta t$, may be approximated with the term: $k_r \cdot \Delta t \cdot \Phi \cdot C_g$. For each grid point, the amounts broken down in the various time intervals were summed. As was expected the greatest amounts were decomposed near to the injection depth, where the fumigant concentrations were highest. The total amount decomposed in a soil profile was approximated with the trapezium rule.

The computations on these disappearance processes were checked by adding the amounts volatilized and decomposed for the 1,3-dichloropropene isomer under consideration. Thus sum had to be approximately equal to the rate of application of the compound. The highest deviations were 3% of the rate.

Because at present only rough estimates for the decomposition rates for 1,3-dichloropropene in soils are available, the results of computations on the disappearance of this fumigant from the root zone are only approximations. The object now is mainly to estimate the importance of the various processes and to find out ways to prevent undesirable side-effects. For fumigation of a sandy soil under rather dry conditions (pF ≈ 3) at 12 °C (Case 1) the balance for *cis*-1,3-dichloropropene was roughly as follows: 75% of the rate disappeared at the soil surface, 10% into deeper layers and 15% was decomposed in soil. Under wetter conditions (pF ≈ 2) these figures may be estimated to be about 60%, 5% and 35%, respectively (Case 42).

With the sandy loam soil near Bant the decomposition rate constant was about 0.20 day^{-1}. At the low organic matter contents involved, the rate of transport by diffusion may also be very high. For simulated Case 44 (cf. Table 13), dealing with comparatively dry conditions (pF ≈ 3), the estimates for *cis*-1,3-dichloropropene were: 55% volatilized at the soil surface, 5% diffused into deeper layers and 40% decomposed. For wetter conditions (pF ≈ 2) the estimated values were:
20%, 1% and 80%, respectively (Case 45). The amount decomposed at the injection depth was then 51 μg per cm^3 soil. The importance of disappearance processes like volatilization and decomposition thus varies considerably with field conditions.

To get an impression of the amounts of 1,3-dichloropropene that may be leached in winter, samples were collected from two fields near Witteveen, Drenthe. Soils were humic sandy and a layer of low water permeability began at a depth of 80 cm. The water discharge from these fields was improved by tile drainage just above the slightly permeable layer. The fumigations were carried out in October 1970 with the usual rate of 250 litres of dichloropropene mixture per hectare.

The first samples of drainage water were taken on 16 December 1970. For *cis* and *trans* 1,3-dichloropropene concentrations were 0.03 and 0.02 $\mu\text{g/cm}^3$, respectively. On 1 February, a few days after much rain fell in the area both the concentrations in the soil and in the drainage water were determined. The highest concentrations in soil were found just underneath the plough layer and the values corresponded with concentrations in the water phase of 0.6 and 1.3 $\mu\text{g/cm}^3$, respectively. In the drainage water concentrations of 0.05 and 0.04 $\mu\text{g/cm}^3$ were present. These concentrations were similar to those in soil at a depth of 70 cm.

Thus, even with shallow tile drainage the concentrations in the leaching water were very low. This transport phenomenon contributed little to the disappearance of the fumigant from the root zone under such conditions. However, when fumigation is carried out late in the autumn under wet conditions large amounts of fumigant are still present in the important leaching period and there will be higher concentrations in the subsoil. To reduce contamination of ground water and surface water, late fumigation should be avoided.

6.4 Reasons for side effects

When there is a low decomposition rate in soil, volatilization at the soil surface is the most important discharge process. This is so for many sandy and peaty soils. A high soil moisture content is the most important limiting factor with respect to the diffusion of the fumigant to the soil surface (cf. sections 5.4.3 and 6.3). In spring 1969, concentrations in some of these soils were measured in triplicate for different depths. A field with a sandy peat on peat profile near Smilde, Drenthe, fumigated on 8 November 1968 under wet conditions, still contained on 31 March 1969 about 5% and 10% of *cis* and *trans* 1,3-dichloropropene, respectively. With humic sandy soils, sampled in the middle of June 1969 the residual amounts were about 1% and 2% of the rate, respectively. In a soil with a peat layer underneath the plough layer these amounts were 3% and 5% of the rate at that time. The highest concentrations were found in the depth range of 20 to 35 cm. When crops such as oats and potatoes are sown in spring in areas with these soils, damage may be caused largely by the original compounds of the dichloropropene fumigant. This type of side-effect can nearly always be prevented by not fumigating under wet conditions late in the autumn. From the concentration measurements for sandy and peaty soils in spring it could be seen that after tillage the concentration in the top layer had fallen to very low levels or was even no longer detectable. Therefore such tillage to plough depth seems very useful for shortening the period with side effects. As volatilization at the soil surface is important the behaviour of fumigant compounds in the atmosphere should be studied further.

There were indications that decomposition rates for *cis* and *trans* 1,3-dichloropropene in soil may be high, particularly in loamy soils. Such a situation was present with the fumigation of the field near Bant, dealt with in Section 5.3.3. In a trial at a field of sandy clay-loam near Tzummarum, Friesland, in August 1969, the soil surface was sealed with plastic sheeting immediately after fumigant injection. A very high disappearance rate was measured, while with a similar trial at a field of humic sandy soil the diffusion pattern was as expected. In the sandy clay-loam, a distinct abnormal odour was still present after the original compounds of the dichloropropene fumigant had disappeared.

Sometimes after fumigation of a loamy soil under rather wet conditions in August, there were problems with crops sown in the following spring, even though dryer periods followed during which the compounds in the dichloropropene fumigant should have disappeared by vapour diffusion. From the computations in Section 6.3 it follows that under comparatively wet conditions about 80% of the *cis*-1,3-dichloropropene applied, could be decomposed in soil. Then high concentrations of the decomposition product may be present near the injection depth. Fumigation of loamy soils under wet conditions should thus be avoided at all costs. Under dryer conditions more fumigant disappears at the soil surface and a more even distribution of the decomposition product throughout the soil is obtained. Still more information is needed about the decomposition rates for 1,3-dichloropropene under various conditions, the nature of decomposition products and their behaviour in soil.

Problems with the growing of sugar and fodder beet, after application of dichloropropene fumigant in autumn, occurred mainly at sites with a poor soil structure and mostly with potatoes-beet successions in the crop rotation scheme. There are examples of sugar-beet growing well with 1,3-dichloropropene residues in the lower part of the plough layer. Until more is known about this problem it is recommended to avoid growing beet after soil fumigation.

The dichloropropene fumigants are complex mixtures consisting mainly of volatile chlorinated hydrocarbons. The same reasoning may be applied to compounds like 1,2-dichloroethane, 1,2-dichloropropane and 2,3-dichloropropene as for the isomers of 1,3-dichloropropene. However, some of the minor admixtures might show a greater deviation from the behaviour of 1,3-dichloropropene in soil, and these compounds should be studied further.

7 General discussion

7.1 Use of computation models in soil fumigation studies

It is interesting to review how the events during soil fumigation with 1,3-dichloropropene are introduced into the computation models. The evaporation rate for the liquid fumigant in soil is high, so that analytical starting solutions of instantaneous sources may be used. The diffusion in the gas phase is the predominant transport process for fumigants like 1,3-dichloropropene. Because the equilibrium between the concentrations in the gas, water and adsorbing phases is established quickly and is reversible, a good approximation is obtained by assuming equilibrium conditions throughout. Furthermore the adsorption-isotherms are linear in the important concentration range. Therefore in these respects the computations need not be more complex.

However, in certain respects the computations have to be adapted for the study of practical situations. Factors such as diffusion geometry, limits of the soil profile, heterogeneities in the soil, changes in the conditions with time and decomposition, may be built in. With extended computer programmes the amounts of fumigant volatilized and decomposed can be computed.

With the computation models, values of the concentration-time integral can be determined for the water phase at various positions in soil. With field trials the analysis of soil samples at a few time intervals is then sufficient so that much work is saved. The mortality percentage of the parasitic nematodes is directly connected with the dose pattern in soil, which is thus the best standard for comparing fumigation effectivity under different conditions.

One of the greatest obstacles with the models of the behaviour of 1,3-dichloropropene in soil was that basic data were missing or only a wide estimation range was available. The data required for the distribution of 1,3-dichloropropene over the phases in soil had to be determined. Starting from literature data on diffusion coefficients for soil samples, the most probable ranges were established, but more accurate approximations for the actual situations had to be obtained by curve-matching. There is still not sufficient information about the decomposition rate under various conditions and about the fumigant dose-nematode mortality relationship.

From situations studied in the field and with the available basic data, other soil fumigations may be simulated. Then the effect of one factor can be isolated from others. In this way the effect of moisture content, temperature and organic matter content on soil-fumigation effectivity was analysed. As a result the real cause of fumigation failures in the past could be traced and recommendations could be improved.

Computation models are also suitable for finding out the nature and seriousness of certain phenomena. By computation it became evident that the presence of large clods in the plough layer produced serious shade effects in the dose pattern. The simulation on the cracks in the soil surface indicated the very unfavourable effect on the position of the iso-dose lines. With the computations on the wet plough layer more insight was obtained on the consequences of the differences in diffusion coefficient for the fumigant in the gas and water phases.

The computation models are also intended to be instruments in further soil fumigation research. They may indicate which types of experiment for 1,3-dichloropropene are still necessary and which aspects deserve most attention. Although the computations were set up for 1,3-dichloropropene it is possible to use them for other soil fumigants and research with other compounds may be carried out much more quickly. Differences in specific needs of application and conditions may be traced in an early stage.

7.2 Conclusions and recommendations with respect to soil fumigation with 1,3-dichloropropene

For a detailed study of soil fumigation with 1,3-dichloropropene the problems had to be grouped. In practice the problems are interrelated. The question is now how the conclusions from the various problem groups may be combined into general recommendations. Some open questions are also mentioned.

Soil moisture condition As far as weather related conditions are concerned, soil moisture content is the most important factor. In dry soils diffusion rate is usually high, so that low values of the concentration-time integral are obtained. In wet soils the release of the fumigant from the injection position is slow so that the concentrations in most of the soil are continuously low. The uneven distribution under wet conditions is another cause for insufficient fumigation of large parts of the soil. For an effective fumigation there must be a well-distributed and continuous system of gas-filled pores in the soil. The situation in the denser parts of the plough layer, like the clods, is critical in this respect.

With soil fumigation under wet conditions undesirable side-effects may occur even after the waiting period. In soils and conditions with low decomposition rates, the components of the dichloropropene mixture may persist over several months and cause damage to crops, even to those sown in spring. With high decomposition rates under wet conditions most of the dichloropropene is decomposed in soil and compounds with presumably high biocidal activity are formed. It is thus essential to avoid soil fumigation under wet conditions, both in view of effectivity and of prevention of undesirable side-effects.

The question now is how to judge the suitability of the soil moisture content for fumigation with 1,3-dichloropropene. From the data on the diffusion of gases and vapours through soil samples and from pF-curves for a number of soils in the Netherlands it follows that the most favourable pF-values may be measured by soil moisture tensiometers. Tensiometers equipped with mercury manometer and ways of removing air are accurate and easy to handle. Thus it seems worth while to test these instruments for the recommendations and to find out the optimum moisture tension range for fumigation of various soils.

Temperature Soil temperature is also an important factor, although less important than soil moisture content. When the soil is rather dry (pF about 3.0 or higher), a high temperature (e.g. 20 °C) is very unfavourable. There are no clear indications that with 1,3-dichloropropene nematode mortalities will be low at temperatures of 7 °C and lower. The fumigant diffusion rate in soil is decreased with decreasing temperature, so that the duration of the period with possible side-effects is increased.

The organic matter content of soil High organic matter content reduces the doses in the soil profile. However, due to the slowing-down of diffusion, the effect is not so great as would be expected on the basis of the adsorption data alone. With a high organic matter content, a thick top layer is insufficiently fumigated. To obtain for peaty sands a nematode mortality equivalent to that for humic sandy soils, a rate about 1.25 times the standard amount of 250 litres dichloropropene mixture (> 50 %) per hectare is necessary. Alternatively as soil moisture content strongly influences the fumigation result, the fumigant could be applied to peaty sands within a more limited moisture range. An increase in fumigant rate is not advisable because strong adsorption increases the risk of aftereffects.

Peat layer at shallow depth It is difficult to fumigate the peat layers that are present underneath peaty sand plough-layers because of poor diffusion and strong adsorption. The rooting in the peat layers with layered structure is also poor so that presumably nematode densities would be low. The fumigant should not be injected into these peat layers because its release from them is very slow and irregular. This results in uneven distribution through the top layer and low doses will be attained in a great part of it. It is best to fumigate a few centimeters above the peat layer, even if the injection depth is less than recommended for normal conditions.

Another consequence of these peat layers is that the compounds remain a long time in the soil, so that there is a great risk of aftereffects, several months after fumigant application in the autumn. In spring the highest concentrations are found in the top of the peat layer.

Preparation of the soil When the soil is not too wet, penetration into dense parts of the soil may be rather good even though the diffusion rate in clods and undisturbed sections of the plough layer is lower than that in the looser parts. An initial period with low concentrations in the dense soil parts is followed by a period with higher concentrations because the disappearance rate is smaller than for the looser parts.

The size of the dense parts has to be restricted because of lower doses on the lee side from the injection position (shade effect). In soils with low decomposition rates, clods of about 7 cm diameter or smaller are allowable. In soils with a high decomposition rate the slowing down of diffusion is very unfavourable and clods should be about 5 cm or smaller. In these situations it is extremely important to finish off the soil surface well because only then is there sufficient time for penetration into the denser soil parts.

When there is about 18 cm between the injection shanks and when dense soil is present in the lower part of the plough layer, the overlap of the pattern of the critical iso-dose lines around the injection lines may be good. Whether the position of these critical iso-dose lines is lower than would be so with a completely loosened plough layer is still a matter for consideration. With distances of 25 cm between shanks that are drawn through dense soil, there are large shade-effects, which decrease fumigation effectivity. Often it is difficult to apply fumigant with shank and blade injectors at sufficient depths when the soil is only prepared to shallow depth.

Soil surface finishing-off It is very important to finish off the soil surface well after fumigant injection. The top centimeters of the soil should be compacted by firm rolling. Irregularities in the soil surface like cracks and protruding clods are very unfavourable. The extra loss in fumigation effectivity may be estimated on the basis of the amount of parasitic nematodes present in the layer with irregularities. The crumbling and levelling of the top layer, compaction by rolling, and avoidance of cracks in the soil surface deserve the full attention of machine engineers, farmers and contractors.

Consequences of a high decomposition rate For loamy soils high decomposition rates for 1,3-dichloropropene were found. This makes the effective fumigation of these soils more difficult. There has to be a rather quick distribution of the fumigant through the soil, because with a slow spread a great part is decomposed near the injection position. Fumigation of rather wet loamy soils is thus very unfavourable. Injection in a dense layer which is only partly disturbed by the fumigation apparatus, is probably also unfavourable. The spreading of the fumigant has to be speeded up by loosening the soil to injection depth with a plough injector or blade injector, or by ploughing before shank injection.

Injection depth Too shallow and too deep injection are both unfavourable. Fumigation is most successful with 1,3-dichloropropene by injecting at depths in the range of 15 to 20 cm. With shank injectors and blade injectors that have a great working-width it is particularly difficult to reach the required depth. The soil must then often be loosened to injection depth beforehand.

Soil fumigation apparatus The various soil fumigation machines may be similarly effective. However an apparatus may have characteristics of design that make it difficult in practice to fumigate successfully. When large amounts of plant residues are present, it is difficult to finish off the soil surface properly with shank and blade injectors. When injection tracks are wide and very loose the penetration into denser soil parts may be insufficient. After plough injection of loamy soils the denser soil displaced to the soil surface may cause problems with the finishing-off. The continuous control of the delivery rate for all the sprayers is an important point. With the present shank injectors this control is not possible and with shanks the risk of blockage is greatest.

Fumigation of the top centimeters of the soil The result of a soil fumigation is very often determined by the thickness of the top layer that is insufficiently fumigated. With the conventional single large-scale field application at low cost there will always be such a layer at least a few centimeters thick. Increases in rate will only result in a limited increase of nematode mortality. To be sure of achieving mortalities of 90% or more, a special procedure is needed to fumigate this top layer. One possibility is split-application, which involves the displacement of the top layer that is insufficiently fumigated the first time, to near the injection depth for the second application. However, more ideal would be a highly effective fumigation in one single operation.

Summary

In arable farming, soil fumigants have become indispensable for the control of plant-parasitic nematodes. Efficiency has to be achieved with low rates, at low cost and with a wide range of soil and weather conditions. At present fumigants containing *cis* and *trans* 1,3-dichloropropene are most frequently used. Research was carried out on the most important causes for failure of soil fumigation, and on how to prevent undesirable side-effects.

With a number of field trials the behaviour of *cis* and *trans* 1,3-dichloropropene was studied. Soil samples were taken from different depths and at different times after fumigant application. The concentrations of fumigant were estimated by using electron-capture gas-chromatography. Soil physical characteristics such as bulk density, organic matter content and moisture content were determined.

Some basic data for the isomers of 1,3-dichloropropene were needed to study the behaviour in soil quantitatively. The coefficients for the distribution over water and air were measured. From adsorption measurements, the extent of adsorption was found to be roughly proportional to the soil organic matter content. The effect of temperature on the distribution coefficients was checked. Literature data on the coefficients for vapour and gas diffusion in soils gave estimation ranges for soil samples in various conditions. There was little information on decomposition rates in soil. From the results of experiments, reported in literature, on the relation between concentration-time product and nematode mortality, the most critical dose range was established.

To describe the diffusion of *cis* and *trans* 1,3-dichloropropene in soil, differential equations were derived for one or two dimensional systems. The variability of the diffusion and adsorption characteristics with position and time was included. For the first hours after fumigant application analytical starting solutions could be used and the solutions dealing with instantaneous sources of the fumigant were suitable. However for most of the fumigation period numerical solutions were used. Explicit difference equations were the most suitable for this purpose. Various forms were derived for the computation of concentrations in grid points, situated in homogeneous layers and near transitions between layers. For the computer calculations FORTRAN programmes were used.

The dose patterns in soil were computed from the basic data and the measured concentrations. From these investigated cases, factors like soil moisture, temperature and organic matter were analysed. The computer models were also used to study the effect and severity of clods in the plough layer, a rough surface and wet conditions during fumigation.

The importance of soil temperature has been overrated in the past. Of the weather related factors, soil moisture is the most important. Many difficulties, connected with both effectiveness and undesirable side-effects, may be avoided by fumigating soils with moisture contents in the favourable range. There is also an optimum range with respect to soil structure; in loose soil (for example produced by rototilling) the diffusion rate is too high and in soil with large clods shade effects in the dose patterns are found. If, after fumigant application, irregularities like clods and cracks are present at the soil surface, then nematode mortality may be considerably lower than when the soil has been well finished off. After careful application with the fumigation equipment used in practice, no clear differences in efficiency were found. Unsatisfactory results with some types of machines in recent years may be attributed to factors like faulty injection depth, stoppage of sprayers and bad finishing-off of the soil surface.

Most of the undesirable side-effects that appear after the waiting period can be prevented by keeping the rate at the present low level, by only fumigating under favourable moisture conditions and by tilling after the fumigation period. However, many questions remain, especially those on decomposition rates in soil and air, and the nature and properties of the decomposition products.

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