

EMISSION OF FUMIGANTS FROM SOIL AND DISPERSION IN AIR



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**EMISSION OF FUMIGANTS FROM SOIL AND DISPERSION IN
AIR**

Proefschrift

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in de landbouw- en milieuwetenschappen,
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Stellingen:

1. De aanname van een bodemsysteem met homogene lagen kan leiden tot een onderschatting van het transport van grondontsmettingsmiddelen in de bodem. Dit proefschrift.
2. Door uitbreiding van een computermodel voor de beschrijving van het gedrag van grondontsmettingsmiddelen in de bodem onder isotherme condities tot een model voor niet-isotherme condities, krijgt men een beter idee van de maxima in de bronsterkte bij de emissie van deze middelen naar de lucht. Dit proefschrift.
3. Het verloop in de tijd van de emissie van methylisothiocyanaat naar de lucht na injectie van metam-natrium in de bodem wordt beter beschreven met een gehalte-afhankelijke snelheidscoëfficiënt voor de omzetting van methylisothiocyanaat in grond dan met een constante snelheidscoëfficiënt. Dit proefschrift.
4. Bij het optreden van temperatuur- en drukverschillen aan het bodemoppervlak kan convectief transport van grondontsmettingsmiddel met de gasfase met name in een droge, grofzandige dan wel in een losgewerkte bouwvoor invloed hebben op de mate van emissie van het grondontsmettingsmiddel naar de lucht. Dit proefschrift.
5. De berekende bronsterkte voor de emissie van de grondontsmettingsmiddelen vanuit de bodem naar de lucht is te onzeker en dient daarom gecontroleerd te worden door metingen van de bronsterkte aan het grondoppervlak. Dit proefschrift.
6. De 6-uurs gemiddelde concentraties van 1,3-dichloorpropeen in lucht liggen over het algemeen een factor 1 000 beneden de MAC-waarde voor de toepasser van deze stof, zodat een bedreiging van de gezondheid van bewoners van gebieden waar 1,3-dichloorpropeen intensief toegepast wordt niet waarschijnlijk is. Dit proefschrift.
7. De richtlijnen van de ISO met betrekking tot de inhoud, vorm en structuur van bibliografische referenties in boeken en tijdschriften dienen beter nageleefd te worden.
Documentation - Bibliographic references - Content, form and structure. International Organization for Standardization. 2nd. ed. No. 690. 1987. 11 p. International Standards. Text in English.
8. Met politiek en emotioneel gemotiveerde beslissingen over de toelating van bestrijdingsmiddelen, die technisch-wetenschappelijk onvoldoende gegrond zijn, bewijst men de maatschappij een slechte dienst.
9. Het aquatisch ecotoxicologisch onderzoek is veelal "bodemloos" en "oeverloos".
10. Het leggen van kwaliteitsnormen voor bestrijdingsmiddelen in drink- en grondwater op de grens van wat analytisch aantoonbaar is, gaat voorbij aan de mogelijkheid van een toxicologische beoordeling van de risico's van de aanwezigheid van deze middelen in het drinkwater.
11. In het kader van de realisatie van de doelstelling in het Meerjarenplan Gewasbescherming om de grondontsmettingsfrequentie terug te brengen naar uiteindelijk ééns in de 5 jaar, dient een eenvoudige toets beschikbaar te komen waarmee vooraf kan worden nagegaan of het gekozen nematicide niet te snel wordt omgezet in de bodem.

12. Modellen ter beschrijving van het gedrag van bestrijdingsmiddelen in de bodem dienen tenminste in enkele representatieve situaties te worden gevalideerd, vóórdát deze modellen gebruikt worden voor beleidsdoeleinden.
13. Het omvormen van DLO tot een marktgerichte organisatie geeft het risico van verlaging van de wetenschappelijke kwaliteit van het uit te voeren onderzoek.
14. Het afwisselend werken aan meerdere projecten, waarbij aan elk van de projecten slechts een beperkte tijd kan worden besteed, vertoont overeenkomsten met de act van de circusartiest die meerdere schoteltjes op de uiteinden van dunne metalen staafjes draaiende probeert te houden; bij een toename in het aantal wordt de kans op een mislukking groter.
15. Het nemen van een beslissing over de toelating van een bestrijdingsmiddel zonder zich rekenschap te geven van de hiaten in de beschikbare informatie en van de gemaakte aannamen bij het schatten van de toxicologische risico's, is niet verantwoord. „The beginning of an acquaintance whether with persons or things is to get a definite outline for our ignorance” - George Eliot in *Daniel Deronda*.
16. De huidige ontwikkeling van het steeds beter afstemmen van de produktie op de behoefte van de consument heeft een negatieve invloed op de creativiteit van de consument. „A mind lively and at ease, can do with seeing nothing, and can see nothing that does not answer”. Jane Austen in *Emma*.
17. In het kader van het werken aan het Europese Huis dient er in het voortgezet onderwijs in tenminste één taal uit elk van de drie grootste talengroepen in Europa, te weten de germaanse, de romaanse en de slavische talengroep, te worden onderwezen. De meest voor de hand liggende keuze om dit te verwezenlijken zou zijn om het Duits te vervangen door het Russisch.
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Stellingen behorend bij het proefschrift van F. van den Berg:
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ABSTRACT

Berg, F. van den, 1992, Emission of fumigants from soil and dispersion in air. Doctoral thesis, Agricultural University, Wageningen, The Netherlands (224 pp.).

In the Netherlands, soil fumigants are used on a large scale for nematode control in arable farming. After injecting the fumigant into the soil, a fraction of the dosage of 1,3-dichloropropene and methyl isothiocyanate (formed from metham-sodium) diffuses up to the soil surface and escapes into the air.

The processes involved in fumigant behaviour in soil are described and the factors affecting these processes are discussed. A standard model including the most important processes is described and used to simulate the fumigation of fields injected with 1,3-dichloropropene or metham-sodium. It was computed that up to a few tens of percent of the dosage of the fumigant can be emitted into the air during the first three weeks after injection.

The impact of several simplifications in the standard model on the rate and extent of emission of fumigant into the air was evaluated. The effect of a fumigant content-dependent rate coefficient for the transformation of fumigant in soil and that of changes in soil moisture content on the rate and extent of emission into the air was computed to be substantial. Although a diurnally changing soil temperature was computed to affect the rate of emission of fumigant into the air substantially, its effect on the cumulative emission in time, compared with a soil system at the average temperature, was computed to be negligible.

Measurements on the one-hour concentrations of methyl isothiocyanate and 1,3-dichloropropene in air were done around two fields injected with metham-sodium and around two other fields injected with 1,3-dichloropropene. Concentrations measured in air were compared with those computed using a gaussian plume model. The comparatively large differences between the computed and measured concentrations in the air during the first few days after injection could be ascribed to an underestimation of the source strength of the emission. Improving the description of the pattern of concentrations of fumigant in air would require more detailed measurements on input parameters for the dispersion model.

In two consecutive years, 6-hour concentrations of 1,3-dichloropropene and methyl isothiocyanate were measured at two locations in a region with intensive use of soil fumigants. For some weeks with many fumigations in this region, the concentration of fumigant in air at a receptor site, with representative fumigated fields at different upwind distances, was computed using a gaussian plume model. The computed and measured concentrations were of the same order of magnitude.

CIP-DATA KONINKLIJKE BIBLIOTHEEK, DEN HAAG

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1 INTRODUCTION

INTRODUCTION

In the last decade, interest in possible harmful effects of toxic organic chemicals in the air on man and the environment has increased substantially. It has been realized that exposure of humans, animals and plants to such chemicals in the air is rather common, although their concentrations show a wide range. A start has been made with the development of criteria and limit values for toxic organic chemicals in air, the ultimate goal being the prevention of harmful effects of such chemicals on man and the environment.

In the Netherlands, a procedure for establishing Maximum Acceptable Concentrations (MAC-values) for occupational exposure to organic chemicals in air has been in operation since 1978 (AI, 1989). The use of MAC-values has been put forward in government policy on protection of the environment. Another limit value is the concentration at which the risk is negligible, and this concentration could be set at 1% of the maximum acceptable concentration (VROM, 1989; VROM et al., 1991). To date, criteria and limit values for air quality have received little attention, compared with those for soil and water quality (VROM & LNV, 1989; VROM et al., 1991). A set of concentration limits for toxic organic chemicals in air representing the maximum and negligible risk levels will be developed. Air quality requirements corresponding to the maximum acceptable risk level should result in the protection of at least humans, common animal species and common plant species against adverse effects (VROM & LNV, 1989).

The establishment of maximum acceptable concentrations is the first priority in government policy on protection of the environment against toxic organic chemicals in air. As immediate application of the most stringent limit values, i.e. those corresponding to a negligible risk, would mean too much strain on economic activities, a step by step approach is followed by using intermediate limit values. The final target is to realize the limit values corresponding to a negligible risk.

Agricultural pesticides constitute an important group of toxic organic chemicals. Nowadays, some 300 pesticides are being used in the Netherlands for agricultural purposes. In the period from 1985 to 1990, annual sales of pesticides, expressed as active ingredient, ranged from 19 400 to 21 500 tons (LNV et al., 1991). The environmental consequences of such large-scale use of pesticides have become a major point of public and political concern.

In the Netherlands, about half the total mass of pesticides used consists of soil fumigants. These fumigants are used to prevent the development of large populations of soil-borne pathogens, especially of plant parasitic nematodes, induced by intensive farming. In the period from 1985 to 1990, annual sales of soil fumigants, expressed as active ingredient, ranged from 9 100 to 11 300 tons (LNV et al., 1991). A large fraction of the soil fumigants (about 76%) is estimated to be used at present for nematode control (especially *Globodera* species) in potato-growing. Smaller fractions

are used in flower-bulb cultures (8%), in outdoor vegetable cultures (7%) and in greenhouse cultures (3 to 6%).

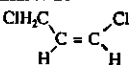
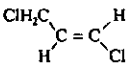
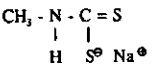
In the arable region of the northeast of the Netherlands, with humic sand and peaty sand soils, which comprises an area of about 1 200 km², many fumigations are done each year. In the eighties, more than 20 000 ha in this region were treated with fumigants each year; the greater part with metham-sodium and the smaller part with 1,3-dichloropropene. The use of metham-sodium tends to be evenly spread throughout the period from September to November. More 1,3-dichloropropene is used later in the autumn because it is considered to be more effective than metham-sodium at lower soil temperatures and in somewhat wetter soils. Until recently, it was mandatory to report the fumigations for potato-growing to the Plant Protection Service in order to obtain permission to cultivate potatoes every two years. Between November 15 and March 15 soil treatments with fumigants are not permitted (with only a few exceptions).

A procedure has been adopted to reduce the use and dosage of fumigants (LNV et al., 1991). From 1993 onwards, the frequency of soil fumigation will be reduced to, at the most, once in four years (with a few exceptions) and from 2000 onwards to at the most once in five years. Preventive soil fumigation, which was usual for intensive potato-growing, will be banned from January 1997 onwards. In future, farmers may have to prove that harmful pathogens in the topsoil of (part of) the field have exceeded a critical level. If so, the farmer would get a prescription from the Plant Protection Service permitting him to buy a certain amount of fumigant. Another measure to reduce the mass of fumigant used is to improve its composition. From 1995 onwards, only the most active isomer of 1,3-dichloropropene, i.e. the (Z)-isomer, can be used.

The dosage of 1,3-dichloropropene (roughly an equal mixture of the (Z)-isomer and the (E)-isomer) applied for nematode control in potatoes is 150 l ha⁻¹. Recently, a product has been approved which contains mainly the (Z)-isomer, which is the component with the highest nematicidal activity. Its dosage for nematode control in potatoes is 100 l ha⁻¹. The dosage of metham-sodium used for nematode control in potatoes is 300 l ha⁻¹ of a 0.51 kg l⁻¹ aqueous solution. Metham-sodium is not volatile, but in the soil it is quickly (largely within a day) transformed into the volatile methyl isothiocyanate. The chemical structure of the soil fumigants 1,3-dichloropropene and methyl isothiocyanate, and that of the fumigant precursor metham-sodium is presented in Table I together with some of their physico-chemical properties.

After being injected at a depth of between 0.15 and 0.20 m, a fraction of the volatile 1,3-dichloropropene and methyl isothiocyanate diffuses up to the soil surface and escapes into the air. Leistra and Frissel (1975) computed that up to about 50% of the dosage of (Z)-1,3-dichloropropene (the more volatile isomer) may enter the atmosphere after being injected into the soil at a depth of between 0.15 and 0.20 m.

Table I : Chemical structure and some physico-chemical properties of (Z)-1,3-dichloropropene, (E)-1,3-dichloropropene, methyl isothiocyanate and the fumigant precursor metham-sodium.

| Chemical compound | Structure | Vapour pressure (kPa) | Solubility in water (g l ⁻¹) |
|-------------------------|---|-----------------------|--|
| (Z)-1,3-dichloropropene |  | 3.3 ^a | 2.7 ^a |
| (E)-1,3-dichloropropene |  | 2.5 ^a | 2.8 ^a |
| methyl isothiocyanate | CH ₃ - N = C = S | 1.7 ^a | 8.9 ^a |
| metham-sodium |  | | 832 ^b |

^a At 20 °C. From Siebering & Leistra (1979).

^b In dihydrate form at 25 °C. From Worthing & Hance (1991).

Fumigant application does not solely result in exposure of contractors and farmers, but may also lead to a certain degree of exposure of people living nearby. In the Netherlands, the maximum acceptable concentration of 1,3-dichloropropene in air, as a time-weighted average for occupational exposures of up to 8 h per day with a maximum of 40 h per week, amounts to 5 mg m⁻³ (AI, 1989). No value has been published so far for the maximum acceptable concentration of methyl isothiocyanate in air for occupational exposure.

There was a serious lack of data on the concentrations of 1,3-dichloropropene and methyl isothiocyanate in air around fumigated fields and at some distance from such fields in residential areas. Such data were needed to evaluate the environmental risk of soil fumigations in the procedure for prolonging the approval of their usage in agriculture. A research programme was set up to estimate the source strength of the emission of fumigants from soil into the air, to compute the patterns of the concentration of fumigants in air around specific fumigated fields as well as in regions with intensive agricultural use of soil fumigants, and to measure the concentrations of the fumigants in air at various distances from fumigated fields.

The rate and extent of the emission of fumigants into the air depend on their spread through the soil after injection. A survey was made of processes and factors which affect fumigant behaviour in soil and this survey is given in Chapter 2. Because of the complexity of fumigant behaviour in soil, suitable simplifications are needed. In Chapter 3, a standard computer model for fumigant behaviour in soil is presented. This model describes the main processes involved in fumigant behaviour, i.e. adsorption onto soil components, partitioning between the liquid and gas phases,

diffusion through the gas-filled pore system and transformation. The fumigation of various fields was simulated with the model. The impact of changes in soil moisture content was estimated by extending the leaching model as developed by Boesten (1986), to include the transport of chemicals through the gas-filled pore system. Further modifications of that model were made to assess the effect of changes in soil temperature.

Methods for sampling and analysis had to be developed to measure the concentrations of the fumigants in air and these are described in Chapter 4. An air sampling programme was set up to collect data on concentrations of fumigant in air around fumigated fields and these measurements are described in Chapter 5 for methyl isothiocyanate and in Chapter 6 for 1,3-dichloropropene. A computer program based on the gaussian plume concept was used to estimate the dispersion of fumigant in air around those fields. In Chapters 5 and 6, the computed concentration patterns are compared with the concentrations measured. In Chapter 7, the influence of soil fumigations in the arable region of the northeast of the Netherlands on the concentrations of fumigants in air in that region is assessed. Finally, in Chapter 8, the implications of the results presented in this thesis are discussed and recommendations are made for further research.

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2 PROCESSES AND FACTORS AFFECTING FUMIGANT BEHAVIOUR IN SOIL

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ABSTRACT

Berg, F. van den, 1992 *Processes and factors affecting fumigant behaviour in soil*, Wageningen (The Netherlands), DLO The Winand Staring Centre. Report 63, 55 pp.; 51 Refs.

The fumigant 1,3-dichloropropene and the fumigant-precursor metham-sodium are usually injected into the soil at a depth of between 0.15 and 0.20 m. In the soil, metham-sodium is transformed into the volatile methyl isothiocyanate. Because of the much higher volatility of fumigants compared with that of most other pesticides, a description of fumigant behaviour in soil should include transport through both the liquid and gas phases. A survey is presented of the processes which may affect fumigant behaviour in soil after injection. The influence of soil and weather factors on the behaviour of fumigant in soil are discussed. A comparison of the influence of the various processes on fumigant behaviour enables the most relevant processes to be identified. Complications in describing fumigant behaviour in soil are discussed and suggestions made for the development of simulation models.

Keywords: soil fumigant, 1,3-dichloropropene, methyl isothiocyanate, metham-sodium, transport, soil surface, formation, transformation, soil temperature, soil moisture

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SUMMARY

Soil fumigants or fumigant precursors are usually injected into the soil at a depth of between 0.15 and 0.20 m. The fumigant 1,3-dichloropropene is injected as a liquid containing a mixture of the (Z)-isomer and the (E)-isomer. Metham-sodium is a fumigant precursor; in the soil it is transformed into the volatile methyl isothiocyanate, which is the actual fumigant. The efficacy of these fumigants to control the development of soil-borne pathogens depends on their spread through the soil as well as on the time they persist in the soil. The rate and extent of emission of fumigants from the soil into the air and the rate and extent of leaching of fumigants into the groundwater also depends on their behaviour in soil.

Fumigants in soil are subjected to various processes, which can be grouped into (trans)formation, partitioning and transport processes. Various soil and weather factors affect these processes. The survey of processes and factors as presented in this report is intended as a starting point for further study on fumigant behaviour in soil, which includes the improvement of computer models to simulate this behaviour. The relative importance of several processes and factors under practical conditions is estimated.

After injection into the soil, more than 90% of metham-sodium is transformed into methyl isothiocyanate, which occurs largely within the first day after injection. It was calculated that at 20 °C it may take up to a few hours before all the injected liquid has vaporized into the gas phase. Partitioning of fumigant between the soil phases results in a shorter time for the liquid fumigant to vaporize. However, at the lower temperatures prevailing in autumn when most soils are fumigated, liquid fumigant may remain for a longer time. The assumptions of instantaneous vaporization and partitioning over the soil phases may not be justified.

Fumigants are transformed in the soil by biological and chemical processes. For 1,3-dichloropropene and methyl isothiocyanate in many soils, the transformation can be described with first-order kinetics. The rate coefficient of transformation is strongly dependent on temperature. In the temperature range of 5 to 35 °C, the rate of transformation is roughly doubled with an increase in temperature of 10 °C.

At equilibrium partitioning between the soil phases, most of the fumigant 1,3-dichloropropene (between 80 and 90%) is adsorbed on the solid phase. A small fraction (less than 1%) is present in the gas phase. The fraction of methyl isothiocyanate in the gas phase is even smaller, because of its higher ratio for the partitioning between the liquid and gas phases. The ratio for the partitioning between the liquid and gas phases is the most sensitive to changes in temperature. When the temperature increased from 2 to 20 °C, the ratio for the partitioning between these phases decreased by about a factor of 3 for both isomers of 1,3-dichloropropene and by about a factor of 2 for methyl isothiocyanate.

Isothermal diffusion of vapour through the gas-phase of the soil system is a result of differences in the concentration of vapour in the gas phase. The contribution of

diffusion in the gas phase to the spreading of fumigant in soil depends on the volume fraction and geometry of the gas phase of the soil. Changes in temperature have comparatively little effect on the coefficient of diffusion of fumigants in air.

Concentration gradients of fumigant in the liquid phase result in diffusion of fumigant through that phase. The coefficient of diffusion of fumigant through the liquid phase is much smaller than the coefficient for the gas phase, so liquid-phase diffusion contributes much less to the spreading of fumigant through the soil than gas-phase diffusion. However, liquid-phase diffusion is essential for the equilibration of fumigant between the soil phases.

Air pressure gradients in the soil cause flow of the gas phase, which results in convective transport of fumigant vapour in this phase. Variations in the velocity of the flow of gas between and within pores increase the spreading of fumigant in soil. Little is known about the contribution of convection to the transport of vapours through the soil. Data in the literature indicate that atmospheric pressure fluctuations cause little gas flow in fine-textured soils, but substantial flow may be caused in coarse-textured soils or in loosely-tilled topsoils. Flow of gas may also occur under a temperature gradient. Possibly, thermal convection is important in dry, coarse-textured soils when the soil surface cools down substantially.

Infiltrating rainwater and evaporation of water at the soil surface results in flow of liquid through the soil system. Flow of liquid containing fumigant results in convective transport of fumigant. The spreading of fumigant in soil is increased by variations in the velocity of the flow of liquid between and within pores. When water infiltrates the soil, the transport of fumigant in soil is predominantly due to convective transport with the liquid phase. Because the ratio for the partitioning of fumigant between the liquid and gas phases is much higher than 1.0, flow of soil air as caused by flow of liquid can be expected to contribute little to the transport of fumigant through the soil.

Temperature may be an important factor when describing fumigant behaviour in soil. Consequently, a description is needed of the course of the temperature in the soil profile with time. The flux densities involved in the heat balance at the soil surface are briefly discussed. Temperature gradients in the soil cause transfer of heat by conduction; its description is complicated by the effect of changes in soil moisture content on the thermal properties of the soil. Transfer of heat may also occur as a result of liquid flow. Further, transport of water vapour may result in substantial flux densities of latent heat. A simpler, empirical description of soil temperatures is also presented.

The combination of effects of changes in soil moisture content and soil temperature on the processes relevant to fumigant behaviour is complicated. A description of all processes and factors would result in a very complex simulation model. Therefore, it is advisable to introduce appropriate simplifications. However, caution is needed because such simplifications are likely to be justified only under certain conditions.

1 INTRODUCTION

The soil fumigant 1,3-dichloropropene and the fumigant precursor metham-sodium are often injected into the soil at a depth of between 0.15 and 0.20 m, using a horizontal-blade type injector with spray nozzles under the blades. The fumigant 1,3-dichloropropene (a mixture of the (Z)-isomer and the (E)-isomer) is injected into the soil as a liquid. Metham-sodium is largely transformed in the soil into the volatile methyl isothiocyanate, which is the actual fumigant. Fumigants have to spread in the soil to be effective against soil-borne pathogens. A description of the spreading of fumigants in soil requires information on their partitioning between the soil phases, on their transport through the soil and on their rate of transformation in soil. These processes determine the rate and extent of the emission of fumigants into the air as well as the rate and extent of their leaching into the groundwater.

Vaporization of the liquid fumigant 1,3-dichloropropene takes some time and as it is an endothermic process, the heat of vaporization is withdrawn from the surrounding soil. The process of fumigant vaporization and the factors influencing it are discussed in Section 2.

After their injection into the soil, fumigant precursors and fumigants are transformed into other compounds. The transformation may be a chemical process, a biological process or a combination of both. The transformation is essential for nematode control when injecting metham-sodium, because its major transformation product, methyl isothiocyanate, is the actual biocidal agent. Transformation of the fumigant decreases the exposure of soil-borne pathogens; if this process is too fast the number of pathogens may not be reduced sufficiently to prevent damage to the following crop. The rate of transformation is affected by the physico-chemical properties of the soil components as well as by the density, activity and composition of the microbial population. Transformation of fumigant precursor and fumigants in soil and the factors affecting the rate of transformation are discussed in some detail in Section 3.

Partitioning of the fumigant over the gas and liquid phases is related to the saturated vapour pressure and the solubility in water. The fraction of fumigant adsorbed on the solid phase depends on the physico-chemical properties of the fumigant and on those of the solid phase. Adsorption of fumigant onto the solid phase is largely determined by the organic matter fraction of the soil. Soil temperature is an important factor in the partitioning of fumigant over the soil phases, as it affects vapour pressure, solubility in water, and adsorption. The partitioning of fumigant over the soil phases and the factors affecting it are discussed in Section 4.

Because of the high volatility of the soil fumigants, compared with that of most of the other pesticides, their spreading in soil by diffusion through the gas phase needs to be considered. Shortly after injection, high concentration gradients occur around the depth of injection. Spreading of fumigant through the soil results in a decrease in the concentration gradients and consequently in a decrease in the diffusion flux

densities. Changes in soil moisture content caused by flow of liquid result in corresponding changes in the gas-filled pore space, thereby affecting the spreading of fumigant by diffusion. Changes in the moisture content in the soil profile may also result from the diffusion of water vapour through the gas phase. Diffusion of fumigant and water vapour through the gas phase and the factors affecting it are discussed in more detail in Section 5. Diffusion of fumigant through the liquid phase is important for attaining equilibrium in the partitioning of fumigant over the soil phases. The diffusion of fumigant through the liquid phase is discussed in Section 6.

A pressure gradient in the gas-filled pore system of the soil causes flow of soil air. Pressure gradients can result from pressure fluctuations at the soil surface and from fluctuations in the groundwater table. Temperature gradients in the soil may also cause flow of soil air. The flow of soil air and the transport of fumigant and water vapour by convection in the gas phase are discussed in some detail in Section 7, together with the factors affecting them. Flow of liquid is induced by rainwater infiltrating the soil or by water evaporating at the soil surface. Because a fraction of the fumigant is in the liquid phase, the flow of this phase contributes to the transport of fumigant in soil. The convective transport of fumigant in the liquid phase is discussed in some detail in Section 8.

Soil temperature influences many processes relevant to fumigant behaviour, e.g. the transformation of fumigant and the partitioning of fumigant over the soil phases. An assessment of the effect of a changing soil temperature on fumigant behaviour requires a description of the transfer of heat through the soil as well as a description of the heat balance at the soil surface. Temperature effects can be expected to be most pronounced in the plough layer, as in this layer daily variations in soil temperature are greatest. Transfer of heat through the soil and the heat balance at the soil surface are discussed in Section 9.

The spreading of fumigant in soil depends on many processes and factors. Therefore, a computer model for its simulation, which takes all the processes and factors into account, will be very comprehensive and complex. Appropriate simplifications could be made by estimating the importance of processes and factors under the prevailing soil and weather conditions. A perspective for the modelling of the behaviour of fumigants in soil is given in Section 10.

2 APPLICATION AND VAPORIZATION OF FUMIGANT

2.1 Application

The fumigant 1,3-dichloropropene is often injected as Telone II or D-D 95, liquids which contain more than 92% of a roughly equal mixture of the (Z)-isomer and the (E)-isomer. The dosage usually applied for nematode control in potato-growing is 150 L ha⁻¹. Recently, a product has been introduced which mainly contains the biologically most active (Z)-isomer, and its dosage for nematode control is 100 L ha⁻¹. The (Z)-isomer is somewhat more volatile than the (E)-isomer, the saturated vapour pressures at 20 °C being 3.3 and 2.5 kPa, respectively (Goring, 1962). Metham-sodium is injected as an aqueous solution (0.51 kg L⁻¹) and the dosage of this solution applied for nematode control in potato-growing is 300 L ha⁻¹. After injection into the soil, metham-sodium is quickly transformed into the volatile methyl isothiocyanate, largely within a day (Smelt et al., 1989a). The saturated vapour pressure of methyl isothiocyanate at 20 °C is 1.7 kPa (Smelt and Leistra, 1974).

2.2 Heat of vaporization

After injection into the soil, the liquid 1,3-dichloropropene vaporizes, which is an endothermic process, the heat of vaporization being withdrawn from the surrounding soil. The molar enthalpy needed for the vaporization of liquid fumigant can be calculated using the Clausius-Clapeyron equation (Waser, 1966):

$$\frac{d \ln (p_{fs})}{dT} = \frac{\Delta H_{f,v}}{R \cdot T^2} \quad (1)$$

in which:

| | | |
|------------------|--|--|
| p_{fs} | = saturated vapour pressure of fumigant | (Pa) |
| T | = temperature | (K) |
| $\Delta H_{f,v}$ | = molar enthalpy of vaporization of fumigant | (J mol ⁻¹) |
| R | = molar gas constant | (J mol ⁻¹ K ⁻¹) |

It should be noted that the logarithm is taken of a dimensionless number, because the saturated vapour pressure as introduced into the equation is divided by one unit of pressure. It follows from this equation that the effect of a change in temperature on the saturated vapour pressure is greater when the enthalpy of vaporization is higher. From the difference between the saturated vapour pressures of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in air at 0 and 20 °C as calculated by Leistra (1972), the molar enthalpies of vaporization can be calculated to be 37 and 38 kJ mol⁻¹ for the (Z)-isomer and the (E)-isomer, respectively. To vaporize 0.081 mol, i.e. the amount of the (Z)-isomer applied per square metre, 3.0 kJ is needed. Because the heat capacity of a soil is in the order of a few MJ m⁻³ K⁻¹, the temperature decrease in a soil layer of 0.01 m thickness would be in the order of

0.1 K. For this reason, the decrease in soil temperature due to vaporization of the fumigant in soil can be neglected.

2.3 Rate of vaporization

The time needed for liquid fumigant to vaporize can be estimated by using the equations derived by Bird et al. (1960) for a diffusion-controlled vaporization process in a semi-infinite system. In this system, vapour A diffuses from the surface of liquid A into gas B in a tube of infinite length. It is assumed that gas B is not soluble in liquid A and that there is equilibrium between liquid A and vapour A at their interface. Further, it is assumed that the temperature and pressure of the system remain constant and that vapour A and gas B form an ideal-gas mixture. The volume of vapour A formed in time interval t after the start is then given by (Bird et al., 1960):

$$V_A = S \cdot \Phi \cdot \sqrt{(4 \cdot D_{A,dif,B} \cdot t)} \quad (2)$$

in which:

| | | |
|---------------|---|---|
| V_A | = volume of vapour A formed | (m ³ (gas)) |
| S | = surface area of vaporization | (m ² (gas)) |
| Φ | = coefficient | (dimensionless) |
| $D_{A,dif,B}$ | = coefficient of diffusion of vapour A in gas B | (m ² (gas) s ⁻¹) |
| t | = time | (s) |

The coefficient Φ equals the velocity at which the mixture of A and B passes a cross section of the tube (perpendicular to the velocity), multiplied by $\sqrt{(t/D_{A,dif,B})}$. This coefficient depends on the equilibrium vapour concentration of A at the interface with liquid A. The magnitude of Φ increases when this concentration increases, as the upward flow of the mixture A and B increases. However, for small values of Φ , the convective transport of A up the tube can be neglected, resulting in the following equation (Bird et al., 1960):

$$V_A = S \cdot F_{A_s} \cdot \sqrt{(4 \cdot D_{A,dif,B} \cdot t/\pi)} \quad (3)$$

in which:

| | | |
|-----------|--|-----------------|
| F_{A_s} | = mol fraction of saturated vapour A in the gas-vapour mixture | (dimensionless) |
|-----------|--|-----------------|

For a mixture of ideal gases, F_{A_s} is equal to the saturated vapour pressure of A divided by the total pressure.

For the (Z)-isomer and the (E)-isomer at 20 °C, F_{A_s} amounts to 0.033 and 0.025, respectively, at a total pressure for the system of 101 kPa. The dosage of Telone II applied for nematode control in potatoes is 150 L ha⁻¹. Using this product, the amount of (Z)-1,3-dichloropropene applied per square metre is 0.081 mol and that for the (E)-isomer is 0.068 mol, corresponding to gas volumes at 101 kPa and 20 °C of $1.95 \cdot 10^{-3}$ and $1.63 \cdot 10^{-3}$ m³, respectively. The diffusion coefficient of 1,3-dichloropropene in air at 20 °C is $8.0 \cdot 10^{-6}$ m² s⁻¹, as estimated using a method

described by Reid and Sherwood (1966). Further, it is assumed that the nitrogen-oxygen mixture in air behaves as an ideal gas. Only a fraction of the soil system is occupied by the gas phase, which results in the coefficients of diffusion being lower in soil than in air. For example, for a soil with a fraction of 0.23 of gas-filled pore volume, the coefficient of diffusion in air should be multiplied by 0.053 (Leistra, 1972). The time needed for a volume of liquid corresponding to that applied per square metre to vaporize can now be calculated and amounts to 107 and 130 minutes for the (Z)-isomer and the (E)-isomer, respectively. Many fumigations are done in late autumn, when soil temperatures are lower than 20 °C. Mainly because F_{Aa} is lower, a longer time is needed for the fumigant to vaporize. Only when assessing the behaviour of 1,3-dichloropropene in soil on a time-scale of several days, is the time of vaporization small compared with the time elapsed since injection.

It should be noted that in the calculation of the time needed for the fumigant to vaporize, the partitioning of fumigant over the soil phases (dissolution, adsorption) was neglected. This partitioning results in a decrease in the concentration of fumigant in the gas phase around the depth of injection, which results in a shorter time for the remaining amount of liquid fumigant to vaporize than calculated. On the other hand, the gas-filled pores in denser or wetter parts of the soil may not all be interconnected. Fumigant vapour may then be trapped, thereby slowing down the rate of vaporization of liquid fumigant. Further, part of the liquid fumigant may dissolve into the soil solution and become adsorbed onto the solid phase before transfer to the gas phase occurs. In comparatively dense and wet soils in particular, the release of fumigant from the depth of injection may be much slower than calculated above.

3 FORMATION AND TRANSFORMATION OF FUMIGANT

In some fumigant applications, a fumigant precursor such as metham-sodium is injected into the soil. Assuming first-order kinetics, the formation of fumigant from a fumigant precursor can be described as:

$$R_{fo} = k_{fo} \cdot C_{p,s} \quad (4)$$

in which:

$$R_{fo} = \text{rate of formation of fumigant} \quad (\text{mol m}^{-3}(\text{soil}) \text{ s}^{-1})$$

$$k_{fo} = \text{rate coefficient of formation of fumigant} \quad (\text{s}^{-1})$$

$$C_{p,s} = \text{concentration of precursor in soil system} \quad (\text{mol m}^{-3}(\text{soil}))$$

After injection of metham-sodium into the soil, it is quickly transformed into methyl isothiocyanate. After application of metham-sodium to soil (at 15 °C) from different fields with moisture contents ranging from 0.10 to 0.40 kg(liquid) kg⁻¹(solid), the maximum amount of methyl isothiocyanate was measured within 1.0 day (Smelt et al., 1989a). They measured the fraction of metham-sodium transformed into methyl isothiocyanate to be higher than 90%. Some caution is needed, as the rate and extent of the transformation of metham-sodium under field conditions may be different from the rate and extent under laboratory conditions. When simulating the fate of methyl isothiocyanate in soil, its formation from metham-sodium may be needed to be taken into account, especially when soil temperatures are low.

In many cases, first-order kinetics is reported to describe transformation of pesticides in soil quite well (Boesten, 1986). The first-order rate equation for the transformation of fumigant is given by:

$$R_{tr} = k_{tr} \cdot C_s \quad (5)$$

in which:

$$R_{tr} = \text{rate of transformation of fumigant} \quad (\text{mol m}^{-3}(\text{soil}) \text{ s}^{-1})$$

$$k_{tr} = \text{rate coefficient of transformation of fumigant} \quad (\text{s}^{-1})$$

$$C_s = \text{concentration of fumigant in soil system} \quad (\text{mol m}^{-3}(\text{soil}))$$

The rate coefficient of transformation depends on soil temperature. This dependency can be described using the Arrhenius equation, which quantifies the effect of temperature on the rate coefficient of chemical reactions. Although there is no theoretical basis for the use of this equation to describe the effect of temperature on the transformation rate of pesticides in soil, it can be used to describe experimental data (Boesten, 1986). Another equation describing the relationship between the rate coefficient and temperature was suggested by Boesten (1986):

$$k_{tr}(T) = k_{tr}(T_0) \cdot \exp\{\Gamma(T - T_0)\} \quad (6)$$

in which:

$$T_0 = \text{reference temperature} \quad (\text{K}) \quad (K)$$

Γ = coefficient

(K⁻¹)

For temperatures between 5 and 35 °C the average value for Γ can be taken as 0.08 K⁻¹ (n = 54, s.d. = 0.02 K⁻¹). This corresponds to an average molar activation energy in the Arrhenius equation of 55 kJ mol⁻¹ (s.d. = 15 kJ mol⁻¹). It can be inferred from these average values that the rate of transformation at 35 °C is 11 times the rate at 5 °C.

The effect of temperature on the first-order rate coefficient of transformation of methyl isothiocyanate in soil was studied by Smelt and Leistra (1974). In a humic sand soil, the rate coefficient at 21 °C was five times that at 4 °C. According to Equation (6), the rate coefficient at 21 °C would be about four times as high. The smaller difference in rate coefficient corresponds to a lower molar activation energy.

The effect of the daily variation in soil temperature on the cumulative amount of fumigant transformed can be demonstrated by comparing the amount transformed after one day calculated for the average soil temperature with that calculated for one day with variable temperature. The initial concentration of fumigant present in the soil is taken as C_0 . It is assumed that the soil temperatures during four consecutive 6-hour periods are 5, 10, 15 and 10 °C, respectively, which results in an average temperature for the whole day of 10 °C. A transformation rate coefficient can be calculated for each of these periods using Equation (6). The concentration of fumigant remaining in soil at 10 °C after one day, with a first-order rate coefficient of 0.070 d⁻¹, equals 0.932 C_0 . The concentration calculated to remain after four 6-hour periods with different temperatures equals 0.930 C_0 . Thus, the assumption of a constant temperature corresponding to the average temperature of the period under consideration gives only a very small deviation in the fraction transformed.

The influence of soil moisture content on the rate of transformation of herbicides has been reviewed by Boesten (1986). He noted that for most studies reported in the literature, the effect of soil moisture on the rate coefficient could be described by the following empirical equation:

$$k_t = A \cdot w^B \quad (7)$$

in which:

A = coefficient

(s⁻¹)

w = soil water content

(kg (liquid))/(kg (solid))

B = exponential coefficient

(dimensionless)

If the coefficient B is taken to be zero, then the rate coefficient is not affected by the soil water content. In the studies on the effect of water content, the contents ranged from that for air-dry soil to that for soil at field capacity. It should be noted that extrapolation to very dry situations may not be justified (Boesten, 1986). The average value for B derived from literature data on herbicides amounted to 0.744 (n = 45, s.d. = 0.482). These literature data did not indicate a correlation between the value of B and herbicide or soil type. No data are available for the influence of

soil moisture content on the rate coefficient for the transformation of 1,3-dichloropropene and methyl isothiocyanate in soil.

In recent years, complications have arisen in the description of the rate of transformation of fumigants in soil. Smelt et. al (1989b,c) measured comparatively high rate coefficients for the transformation of 1,3-dichloropropene at low contents in soil. Further, enhanced transformation of the soil fumigants 1,3-dichloropropene and methyl isothiocyanate in soil after a certain initial period has been reported by Smelt et al. (1989a, b and c). This implies that for those soils the rate of transformation can no longer be approximated with only first-order kinetics. Presumably, there are species of microorganisms in soil which adapt their enzyme production, and this results in transformation of fumigant at an enhanced rate. The duration of the initial period was found to vary significantly between different soils. The enhanced transformation of fumigant may be induced by repeated fumigant applications. However, in one soil no accelerated transformation of the fumigant was measured even after 13 applications. The uncertainties in the occurrence of enhanced transformation of fumigant and in the duration of the preceding time interval may make the description of the transformation of fumigant in soil difficult.

4 PARTITIONING OF FUMIGANT BETWEEN THE SOIL PHASES

For the adsorption of fumigant from the liquid phase onto the solid phase, the most simple equilibrium model is based on linear adsorption and can be described as:

$$X = K_{sl} \cdot C_l \quad (8)$$

in which:

X = amount of fumigant adsorbed per unit mass of soil (mol kg⁻¹ (solid))

K_{sl} = ratio for the partitioning of fumigant between solid and liquid phases
(mol kg⁻¹ (solid))/(mol m⁻³ (liquid))

C_l = concentration of fumigant in the liquid phase (mol m⁻³(liquid))

This type of adsorption model was commonly used in the modelling of fumigant behaviour in soil (Leistra, 1972; Siebering and Leistra, 1979; Wagenet et al., 1989; Leistra and Crum, 1990). Another equation which has been used (Calvet, 1980; Boesten, 1986; Boesten et al., 1989; Boesten, 1991; Boesten and Van der Linden, 1991) to describe the equilibrium adsorption of pesticides onto soil is the Freundlich equation. If the Freundlich exponent equals unity, the equation becomes the same as Equation (8). Other descriptions of the adsorption have also been used for pesticides, e.g. the Langmuir equation (Cohen et al., 1988). Weber and Miller (1989) presented a classification of adsorption isotherms in their review of the types of isotherms for different pesticides and adsorbents.

Because of the volatility of the fumigants, a significant fraction of these chemicals is present in the gas phase of the soil system. The relation between the concentrations of fumigant present in the liquid and gas phases (for dilute solutions) can be described by:

$$C_l = K_{lg} \cdot C_g \quad (9)$$

in which:

K_{lg} = ratio for the partitioning of fumigant between liquid and gas phases
(mol m⁻³ (liquid))/(mol m⁻³ (gas))

C_g = concentration of fumigant in the gas phase (mol m⁻³(gas))

It should be noted that K_{lg} equals the inverse of the dimensionless form of Henry's constant (Jury and Ghodrati, 1989).

In the linear sorption model at equilibrium, the amount of fumigant in the gas phase is also related to the amount adsorbed on the solid phase:

$$X = K_{sl} \cdot K_{lg} \cdot C_g \quad (10)$$

Although the saturated vapour pressures of the fumigants are very high compared with those of most pesticides, the fraction of the fumigant 1,3-dichloropropene present

in the gas phase at temperatures of between 2 and 20 °C was calculated to be less than 1% (Leistra, 1972). The largest fraction, between 80 and 90%, was calculated to be adsorbed onto the solid phase.

At low soil moisture contents, i.e. below a few percent, pesticides are adsorbed very strongly onto soils (Taylor, 1978; Taylor and Spencer, 1991). Under such conditions, the cover of the surface of the solid phase with water molecules is incomplete. As more adsorption sites are then available for pesticide molecules, a greater fraction of pesticide is adsorbed onto the solid phase.

The influence of temperature on the partitioning of fumigant between the solid and liquid phases can be described using the Van 't Hoff equation. This equation describes the temperature dependence of the equilibrium constant of a chemical reaction (Waser, 1966). After integration, the relationship between the equilibrium constant $K_{s/l}$ and temperature is described by:

$$K_{s/l}(T) = K_{s/l}(T_0) \exp \left[\frac{-\Delta H_s}{R} \left\{ \frac{1}{T} - \frac{1}{T_0} \right\} \right] \quad (11)$$

in which:

ΔH_s = molar enthalpy of adsorption of fumigant on the solid phase ($J \text{ mol}^{-1}$)

Equation (11) has been used by Padilla and Lafrance (1988) to calculate the equilibrium constant for the adsorption of atrazine onto the solid phase at different temperatures. It has also been used by Streile (1984) to calculate the linear adsorption coefficient for the adsorption of napropamide and lindane on a sandy loam soil at different temperatures. For example, the linear adsorption coefficient for lindane was calculated to decrease by a factor of 2 when the temperature increased from 2 to 20 °C, which implies a negative value for ΔH_s .

The effect of temperature on the partitioning of 1,3-dichloropropene between the solid and liquid phases has been studied by Leistra (1972). The dependence of $K_{s/l}$ on the temperature was estimated to be comparatively small. The values of $K_{s/l}$ of both isomers of 1,3-dichloropropene for a humic sandy soil were estimated to increase by a factor of 1.3 when the temperature increased from 2 to 20 °C. This would result in a positive value for the molar enthalpy of adsorption for 1,3-dichloropropene.

Bowman and Sans (1985) described the effect of temperature on the solubility of insecticides in water. The equation they used can be obtained by substituting in Equation (11) the equilibrium constant $K_{s/l}$ by the solubility of the chemical compound S_c (expressed as a mol fraction), and the molar enthalpy of adsorption ΔH_s by the molar enthalpy of dissolution of the chemical compound in water ΔH_d . Using their data on the molar enthalpy of dissolution of insecticide, the average molar enthalpy of dissolution is calculated to be about 30 kJ mol^{-1} ($n=29$, s.d.= 33). This would result in the solubility at 20 °C to be about 2.3 times higher than at 2 °C.

The effect of temperature on the solubility of 1,3-dichloropropene in water has been studied by Leistra (1972). This effect was estimated to be comparatively small: the solubility decreased by a factor of about 1.3 when the temperature increased from 2 to 20 °C. This relation between solubility and temperature implies a negative molar enthalpy of dissolution in water, whereas Bowman and Sans (1985) determined a positive molar enthalpy of dissolution in water for most of the insecticides they studied.

For the temperature dependence of the partitioning of an organic compound between the liquid and gas phases, an equation similar to Equation (11) has been used (Streile, 1984; Kerfoot, 1991). It was used by Streile (1984) to describe the influence of temperature on the partitioning of lindane between the liquid and gas phases. The value of K_{lg} was calculated to decrease from about 100 to 14 (about a factor of 7) when the temperature increased from 2 to 20 °C.

The effect of temperature on the partitioning of 1,3-dichloropropene between the liquid and gas phases has been assessed by Leistra (1972). The partition ratio K_{lg} for the (Z)-isomer decreased from 59 to 18 (about a factor of 3) when the temperature increased from 2 to 20 °C. A similar decrease was measured for the (E)-isomer. The partitioning of 1,3-dichloropropene between the liquid and gas phases is less sensitive to changes in temperature than that of lindane, which can be explained by a higher molar enthalpy for the volatilization of lindane from the aqueous into the gas phase than that of 1,3-dichloropropene.

The effect of temperature on the partitioning of methyl isothiocyanate between the soil phases has been studied by Smelt and Leistra (1974). Similar to 1,3-dichloropropene, K_{lg} is the partition ratio most sensitive to changes in temperature. The partition ratio K_{lg} was measured to decrease from 330 to 170 when the temperature increased from 4 to 20 °C.

The effect of temperature on the partitioning of fumigant between the soil phases is rather complex, because it is a combination of the effects of temperature on the adsorption of fumigant onto the solid phase, on the solubility of the fumigant in the liquid phase and on the saturated vapour pressure of fumigant.

5 DIFFUSIVE TRANSPORT IN THE GAS PHASE

5.1 Fumigant

Differences in concentration of fumigant in the gas phase of the soil system with depth result in the diffusion of fumigant through that phase in the direction of decreasing concentration. The one-dimensional flux density of fumigant by diffusion through the gas phase of the soil system in the vertical direction is described by:

$$J_{f,dif,g} = - D_{f,dif,g} \frac{\partial C_g}{z} \quad (12)$$

in which:

$J_{f,dif,g}$ = flux density of fumigant by diffusion through the gas phase
(mol m⁻²(soil) s⁻¹)

$D_{f,dif,g}$ = coefficient of diffusion of fumigant in the gas phase
(m³(gas) m⁻¹(soil) s⁻¹)
 z = depth in soil (m(soil))

The diffusion coefficient of a gaseous compound in soil depends on the gas-filled pore volume of the soil system. Moreover, this coefficient needs to be corrected for the tortuosity of the pore system. Hence:

$$D_{f,dif,g} = D_{f,dif,a} \cdot \tau_g \cdot \Theta_g \quad (13)$$

in which:

$D_{f,dif,a}$ = coefficient of diffusion of fumigant in air (m²(gas) s⁻¹)
 τ_g = tortuosity factor for diffusion in the gas phase (m²(soil) m⁻²(gas))
 Θ_g = volume fraction of the gas phase (m³(gas) m⁻³(soil))

The tortuosity factor depends on the volume fraction of the gas phase of the soil system. Experimental values for this factor have been compiled by Leistra (1972). In the estimation method used by Wagenet et al. (1989), the tortuosity factor is a function of total porosity and volume fraction of the air-filled pore space.

High concentrations of fumigant in the gas phase can be expected around the depth of injection. At the interface of the liquid fumigant and the soil air, the concentration of fumigant in the gas phase will correspond to the saturated vapour pressure of fumigant at the prevailing soil temperature. It takes time for liquid fumigant to vaporize (see Section 2.3), and as long as liquid fumigant is present, comparatively high concentration gradients will develop around the injection depth and consequently the flux density of diffusion of fumigant can be expected to be high. Thereafter, diffusion flux densities decrease because the spreading of fumigant to surrounding soil layers results in lower concentration gradients.

The dependency of the diffusion coefficient in air on temperature, e.g. for 1,3-dichloropropene, can be calculated using estimation methods presented by Reid and Sherwood (1966) and by Cohen et al. (1988). The influence of temperature on the coefficient of diffusion of 1,3-dichloropropene in the gas phase, using a Reid and Sherwood method, was comparatively small. The coefficient increased from $7.6 \cdot 10^{-6}$ to $8.0 \cdot 10^{-6} \text{ m}^2 \text{ s}^{-1}$ when the temperature increased from 10 to 20 °C.

The conservation equation for fumigant in soil, with diffusion through the gas phase of the soil system as the only transport mechanism, is given by:

$$\frac{\partial C_s}{\partial t} = - \frac{\partial J_{f,dif,g}}{\partial z} + R_{fo} - R_r \quad (14)$$

In models describing the transport of organic chemicals through the gas phase of the soil system, it is generally assumed that this transport is only due to diffusion (Leistra and Frissel, 1975; Jury et al., 1983; Boesten and Leistra, 1983; Jury and Ghodrati, 1989). Moreover, in models for fumigant behaviour, its transport through the soil was assumed to be only by diffusion through the gas phase (Leistra, 1972; Siebering and Leistra, 1979; Leistra and Crum, 1990).

5.2 Water

The density of water vapour in the gas phase depends on temperature as well as on soil water pressure. Differences in water vapour density due to temperature or soil moisture pressure gradients result in diffusion of water vapour towards places with lower vapour density. The flux density of water vapour diffusion through the gas-filled pore system in the vertical direction can be described by:

$$J_{w,dif,g} = - D_{w,dif,g} \frac{\partial \rho_{w,g}}{\partial z} \quad (15)$$

in which:

$J_{w,dif,g}$ = flux density of water vapour by diffusion through the gas phase
($\text{kg m}^{-2}(\text{soil}) \text{ s}^{-1}$)

$D_{w,dif,g}$ = coefficient of diffusion of water vapour in the gas phase
($\text{m}^3(\text{gas}) \text{ m}^{-1}(\text{soil}) \text{ s}^{-1}$)

$\rho_{w,g}$ = density of water vapour in the gas phase
($\text{kg m}^{-3}(\text{gas})$)

Assuming water vapour to behave as an ideal gas, the water vapour density can be calculated from the water vapour pressure. The increase in the saturated water vapour pressure with increasing temperature can be described by the Clausius-Clapeyron equation. In the derivation of Equation (1), it has been assumed that in the liquid - vapour system the decrease in the volume of the liquid phase upon vaporization is negligible compared with the corresponding increase in the volume of the gas phase.

For water contents in soil higher than those corresponding to the permanent wilting point, the gas phase in the soil is practically saturated with water (e.g. Ten Berge, 1986). Only when the water content becomes lower than that corresponding to the permanent wilting point, does the relative humidity decrease to values distinctly below 1.0. The following equation can be given for the dependence of water vapour pressure on soil moisture pressure (Koorevaar et al., 1983):

$$\ln \frac{p_w}{p_{ws}} = \frac{M}{R \cdot T \cdot \rho_{w,l}} (p_t - p_o) \quad (16)$$

in which:

p_w = actual water vapour pressure (Pa)
 p_{ws} = saturated water vapour pressure (Pa)
 M = molecular mass (kg mol⁻¹)
 $\rho_{w,l}$ = density of liquid water (kg m⁻³(liquid))
 p_t = tensiometer pressure (Pa)
 p_o = osmotic pressure (Pa)

The conservation equation for water in soil by diffusion of water vapour through the gas phase of the soil system is given by:

$$\left[\frac{\partial c_w}{\partial t} \right]_{\text{dif,g}} = - \frac{\partial J_{w,\text{dif,g}}}{\partial z} \quad (17)$$

in which:

c_w = water concentration in the soil system (kg m⁻³(soil))

The contribution of water vapour diffusion to the transport of water is negligible in that part of the soil where diurnal temperature fluctuations are small (Hillel, 1980). However, the contribution of water vapour diffusion may be greater in the surface soil layer. As water vapour diffusion tends to go from warm to cold parts of the soil, this would imply a downward movement during the day and an upward movement during the night (Hillel, 1980). Because of the comparatively large amount of heat required for the evaporation of water, i.e. 44 kJ mol⁻¹ at 20°C (Van Wijk and De Vries, 1963a), significant amounts of latent heat may be transported along with the transport of water vapour through the soil by diffusion. Subsequent condensation of water vapour in a layer with a lower temperature results in a release of this latent heat causing an increase in the temperature of that layer.

Diffusion of water vapour through the soil has been included in the model developed by Ten Berge (1986) to describe the transport of water through the soil. The quantification of the water vapour density flux is complicated by possible evaporation of water from the liquid phase or condensation of water vapour along with the diffusion of water vapour through the gas phase. The transport of water vapour has been measured to be higher than that estimated from diffusion alone (Ten Berge, 1986). One explanation may be the condensation of water vapour at one end of a

liquid water barrier ("liquid island") in a soil pore and the subsequent evaporation of water at the other end. Therefore, Ten Berge (1986) introduced an effective coefficient of diffusion of water vapour to describe the water vapour density flux. Values for the conversion of the coefficient of diffusion of water vapour in air to that in the soil system as compiled by Ten Berge (1986) for sand, loam and silt loam soils were mostly in the range of 1.0 to 3.0. This implies that the enhancement of water vapour transport more than compensates for the decrease in the coefficient of diffusion due to the volume fraction of the gas phase and the tortuosity factor of the soil system.

6 DIFFUSION OF FUMIGANT IN THE LIQUID PHASE

Transport of fumigant in the liquid phase can occur by diffusion because of a gradient in its concentration in the liquid phase. The one-dimensional flux density of fumigant by diffusion through the liquid phase of the soil system in the vertical direction is described by:

$$J_{f,dif,l} = - D_{f,dif,l} \frac{\partial C_l}{\partial z} \quad (18)$$

in which:

$J_{f,dif,l}$ = flux density of fumigant by diffusion through the liquid phase
(mol m⁻²(soil) s⁻¹)

$D_{f,dif,l}$ = coefficient of diffusion of fumigant in the liquid phase
(m²(liquid) s⁻¹)

The coefficient of diffusion of fumigant through the liquid phase can be calculated by:

$$D_{f,dif,l} = D_{f,dif,w} \cdot \tau_l \cdot \Theta_l \quad (19)$$

in which:

$D_{f,dif,w}$ = coefficient of diffusion of fumigant in water (m²(liquid) s⁻¹)

τ_l = tortuosity factor for diffusion in the liquid phase (m²(soil) m⁻²(liquid))

Θ_l = volume fraction of the liquid phase (m³(liquid) m⁻³(soil))

The tortuosity factor for diffusion in the liquid phase depends on the volume fraction of liquid in soil. Values for this factor have been compiled by Leistra (1978). Wagenet et al. (1989) used an empirical exponential function to calculate the coefficient of diffusion in the soil system from the coefficient of diffusion in water and the volume fraction of the liquid phase in soil.

The coefficient for fumigant diffusion in water, $D_{f,dif,w}$, is about 10⁻⁴ times that for fumigant diffusion in air, $D_{f,dif,a}$. In most soils, the values of the volume fraction and the tortuosity factor for the liquid and gas phases are of the same order of magnitude. Hence, the coefficient for fumigant diffusion in the liquid phase, $D_{f,dif,l}$, is about 10⁻⁴ times the coefficient for fumigant diffusion in the gas phase, $D_{f,dif,g}$, so it can be concluded that the diffusion of fumigant through the liquid phase is much slower than that through the gas phase.

In the screening model (Behaviour Assessment Model) developed by Jury et al. (1983), a value of 5.0·10⁻¹⁰ m² s⁻¹ (at 25 °C) for the coefficient of diffusion in water was taken to be representative of all pesticides. At 20 °C, the coefficient of diffusion of 1,3-dichloropropene in water is calculated to be about 8·10⁻¹⁰ m² s⁻¹, which is distinctly higher than the average value taken by Jury et al. (1983). This difference

can be explained by the fact that the 1,3-dichloropropene molecule is smaller than most of the other pesticides.

The conservation equation for fumigant in soil, with diffusion through both the liquid and gas phases, is obtained by inserting the divergence of the diffusion flux in the liquid phase into Equation (14):

$$\frac{\partial C_s}{\partial t} = - \frac{\partial J_{f,dif,g}}{\partial z} - \frac{\partial J_{f,dif,l}}{\partial z} + R_{fo} - R_{lr} \quad (20)$$

As the rate of diffusion of fumigant through the liquid phase is much lower than that through the gas phase, the second term on the right-hand side of Equation (20) was usually neglected in models for fumigant behaviour. This has been done by e.g. Leistra and Crum (1990) in their model for the behaviour of methyl isothiocyanate in greenhouse soil.

7 CONVECTIVE TRANSPORT IN THE GAS PHASE

7.1 Flow of the gas phase

Flow of the gas phase occurs when there is a pressure gradient in the gas-filled pore system. A pressure gradient may arise as a result of changes in atmospheric pressure at the soil surface or of wind blowing over the soil surface. The flow of gas under a pressure gradient through a one-dimensional soil system can be described by (Koorevaar et al., 1983):

$$J_g^v = -K_a \frac{\partial p}{\partial z} \quad (21)$$

in which:

$$\begin{aligned} J_g^v &= \text{volume flux density of gas flow} && (\text{m}^3 \text{ (gas) m}^{-2} \text{ (soil) s}^{-1}) \\ K_a &= \text{air conductivity of the soil} && (\text{m}^3 \text{ (gas) m}^{-1} \text{ (soil) Pa}^{-1} \text{ s}^{-1}) \\ p &= \text{pressure in gas phase} && (\text{Pa}) \end{aligned}$$

Air conductivity depends on the characteristics of the gas-filled pore system: volume fraction of gas-filled pores, size distribution of the pores, continuity of the pores, and geometry of the pores (Koorevaar et al., 1983). The intrinsic permeability of the soil, i.e. air conductivity of the soil multiplied by the dynamic viscosity of air, varies with the type of soil: from about $2 \cdot 10^{-11} \text{ m}^2$ for a dune sand soil (Hoeks, 1972) to $1 \cdot 10^{-14} \text{ m}^2$ for a loam soil (Metcalf and Farquhar, 1987).

Flow of gas through the soil may also be caused by infiltration of rainwater or by a change in the depth of the groundwater table. With rainwater infiltrating the soil, the convective volume flux density of gas can be expected to approach the convective volume flux density of liquid, but with an opposite sign.

The effect of changes in atmospheric pressure at the soil surface on the flow of gas through the soil may be neglected when modelling convective transport of gases in soil layers sufficiently below the soil surface, e.g. below 0.5 m. This has been done in a study on the spreading of methane through the soil as caused by a leak at about 0.8 m below the soil surface (Hoeks, 1972) and also in a study on the spreading of methane in a soil profile of 9 m thickness (Metcalf and Farquhar, 1987). However, close to the soil surface, pressure variations can have an effect on the flow of gas through the soil. This has been demonstrated by Kimball and Lemon (1971), who measured the heptane flux through a 0.02 m layer of different texture. For root mean square pressure fluctuations at the soil surface ranging from 0 to a few Pa, a significant correlation was found between heptane vaporization flux density and air pressure fluctuations for straw and coarse gravel, whereas no significant effect was found for silt loam. The results obtained when using a fan to increase turbulence over the soil surface layer indicate that for mean wind speeds higher than 5 m s^{-1} (at about 4 m above the soil surface) air turbulence may even affect the heptane vaporization

flux density for a silt loam. Equations to describe the effect of pressure fluctuations on the velocity and displacement of soil air have been presented by Kimball and Lemon (1972), but their equations were not tested with measurements.

A temperature gradient in the soil may cause instability of the soil air, which results in thermal convection in the gas-filled pore system. This type of convective transport of gas may occur when there are clear skies during the night. Under such conditions, the temperature at the soil surface decreases, resulting in a reversed temperature gradient, i.e. an increase in temperature with soil depth. To determine whether thermal convection can contribute to the transport of vapour through the gas-filled pore system, the Rayleigh number has been used. The Rayleigh number represents the ratio of the effect of buoyancy to the combined effects of the exchange of heat in the soil and the friction on air flow in the soil. Buoyancy is a vertical movement of air parcels, the parcels having a temperature which differs from that of their surroundings. The occurrence of thermal convection could be indicated by the value of the Rayleigh number for a particular soil system; if it exceeds a critical value convection cells develop with circulating air in each cell (Menenti, 1984). However, it is difficult to determine the critical value of the Rayleigh number for a specific soil system above which thermal convection of soil air occurs (Menenti, 1984; Ten Berge, 1986). Its value depends on the boundaries of the soil system chosen as well as on whether or not the boundary layers are pervious to air flow. Menenti (1984) noted that the theory used to calculate the critical Rayleigh number is based on a constant temperature gradient between the soil system boundaries. Although the temperature at a depth of below 0.5 m in soil may be considered constant on a time scale of days, the temperature at a system boundary between this depth and the soil surface shows a diurnal pattern and its amplitude increases towards the soil surface.

Parameters in the equation to calculate the Rayleigh number as used by Nield (1968), Menenti (1984) and Cohen et al. (1988) are, for example, the intrinsic soil permeability in the numerator and the thermal conductivity in the denominator. Because the permeability depends on factors such as pore size distribution and pore continuity, and the thermal conductivity of a soil depends on moisture content and soil composition, the value of the Rayleigh number for a specific topsoil may show large differences as a result of the infiltration of rainwater or tilling practices. Thermal convection is more likely to occur in dry, loosely tilled soils containing large air voids than in denser and wetter soils.

Cohen et al. (1988) presented a one-dimensional model to compute the flow of the gas phase by thermal convection in nearly dry soils. Their description of thermal convection is extensively simplified. First, for a description of thermal convection a two-dimensional soil system needs to be considered, because of the air circulating within the convection cells. Second, the boundary conditions they imposed upon the system were not realistic, as they resulted in downward convection when the temperature decreased with increasing depth in soil. However, their model can be used to estimate the order of magnitude of the velocity of the gas phase when the temperature increases with increasing depth in soil.

7.2 Convection of fumigant

Flow of air through the soil as caused by factors discussed in the previous section implies that the soil air can act as a carrier for the transport of fumigant through the gas phase. Transport of fumigant by convection of the gas phase can be described by:

$$J_{f,c,g} = J_g^v \cdot C_g \quad (23)$$

in which:

$J_{f,c,g}$ = flux density of fumigant by convection of the gas phase
(mol m⁻²(soil) s⁻¹)

Because the gas-filled pore space consists of pores with different diameters, variations in flow velocity will occur when air flows through the soil system. These differences in flow velocity as well as differences in flow velocity within the pores result in an increased spreading of fumigant. This convective dispersion of fumigant during transport through the gas-filled pore system can be described by:

$$J_{f,dis,g} = - D_{f,dis,g} \frac{\partial C_g}{\partial z} \quad (24)$$

in which:

$J_{f,dis,g}$ = flux density of fumigant by dispersion in the gas phase
(mol m⁻²(soil) s⁻¹)

$D_{f,dis,g}$ = coefficient of convective dispersion of fumigant in the gas phase
(m³(gas) m⁻¹(soil) s⁻¹)

Assuming the dispersion coefficient to be proportional to J_g^v (Metcalf and Farquhar, 1987), it follows that:

$$D_{f,dis,g} = L_{f,dis,g} \cdot |J_g^v| \quad (25)$$

in which:

$L_{f,dis,g}$ = dispersion length for convection of fumigant in the gas phase (m(soil))

When including convection and dispersion of fumigant through the gas phase of the soil system in conservation Equation (20), the new conservation equation becomes:

$$\frac{\partial C_g}{\partial t} = - \frac{\partial J_{f,dif,g}}{\partial z} - \frac{\partial J_{f,dif,l}}{\partial z} - \frac{\partial J_{f,c,g}}{\partial z} - \frac{\partial J_{f,dis,g}}{\partial z} + R_{fo} - R_{fr} \quad (26)$$

A model for the transport of gases by convection and diffusion has been given by Metcalfe (1982) and Metcalfe and Farquhar (1987). They simulated the movement of methane from a waste disposal site over distances of about 30 m through the soil

under a pressure gradient of about 10 Pa m^{-1} . They included the convective dispersion of methane in the gas phase and assigned values to the longitudinal and lateral dispersion lengths of 1.0 and 0.1 m, respectively, as first estimates (Metcalf, 1982). A sensitivity analysis for the model showed that the effect of convective dispersion was only substantial compared with diffusion in gravel or coarse sand layers.

The importance of convective dispersion versus diffusion when describing the transport of a chemical compound in soil can be judged from the value of the Péclet number (Bolt, 1979). When comparing convective dispersion of fumigant in the gas phase with diffusion of fumigant in the gas phase, the Péclet number equals the volume flux density of gas flow, J_g^V , multiplied by the dispersion length, $L_{f,dia,g}$, and divided by the actual diffusion coefficient, $D_{f,dif,g}$. Low values for the Péclet number, i.e. less than 0.01 imply that the effect of convective dispersion on transport is negligible compared with diffusion. Values of the Péclet number greater than 10 indicate that convective dispersion has a greater effect on the spreading of vapour than diffusion. Computations by Metcalfe (1982) on the effect of convective dispersion on vapour transport in soil thus imply comparatively high Péclet numbers for the soil layers consisting of coarse sands or gravel and comparatively low Péclet numbers for soil layers with finer texture.

Enhancement of the transport of vapour through the gas-filled pore system by convection due to pressure fluctuations at the soil surface is sometimes expressed as a multiplication factor of the coefficient of diffusion. Factors of 2 to 4 for 5 mm aggregates and a factor of 100 for coarse mulches consisting of 10 mm aggregates have been reported in the literature (Ten Berge, 1986). For soil materials consisting of granules smaller than 1 mm, Ten Berge (1986) found a value in the literature of 1.0, but gave no details on the amplitude and frequency of the pressure fluctuations.

In a study on the spreading of the fumigant 1,2-dibromo-3-chloropropane in a clay loam soil, Wagenet et al. (1989) considered convective gas transport caused by air pressure fluctuations and groundwater table fluctuation (forced convection). However, they did not describe the processes contributing to convection separately, but included their effect in an effective diffusion coefficient. Wagenet et al. (1989) estimated the enhancement of the coefficient of diffusion through the air-filled pore space by air pressure fluctuations of 2.5 kPa at a frequency of 0.25 d^{-1} and groundwater table fluctuations with an amplitude of 1 m at a frequency of 1 yr^{-1} . They arrived at values of $1.5 \cdot 10^{-6}$ and $1.2 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$, respectively. The values for the coefficient of diffusion of 1,3-dichloropropene in soil can be expected to be of the same order of magnitude (see Section 2.3). As values for the enhancement of diffusion due to pressure and water table fluctuations are assumed not to be dependent on the air-filled pore space, the estimated transport of vapour as caused by such fluctuations may become more important than vapour diffusion when the volume fraction of the gas phase decreases.

An indication of the order of magnitude of the effect of thermal convection on the transport of vapour through the gas-filled pore system in a nearly dry silt loam (moisture content about 4%) was obtained by Cohen et al. (1988). In their model the transport mechanisms considered for lindane were diffusion and thermal

convection in the gas phase. Transformation of lindane in the soil was neglected. They computed the amount of lindane volatilized after its incorporation to a depth of 0.10 m. During the first day (at about 25 °C), about 0.3% of the lindane was computed to be lost by volatilization under isothermal conditions and this fraction increased to 2.0% during the following nine days. Under non-isothermal conditions with an amplitude of the temperature at the soil surface of about 10 K, the fractions of lindane computed to be lost by volatilization were 0.5 and 2.2% at 1 and 10 days after incorporation, respectively. The difference between the percentages of lindane volatilized from the isothermal and non-isothermal soil systems developed during the first day and this was ascribed mainly to the non-linearity of the coefficients of diffusion and adsorption with temperature. Thus, the effect of thermal convection on the loss of lindane by volatilization after its incorporation into the soil was estimated to be small.

7.3 Convection of water

When soil air is flowing, the water vapour present in the gas phase is transported along with it. The expression for the transport of water vapour with the gas phase is similar to that for the transport of fumigant by this mechanism and is described by:

$$J_{w,c,g} = J_g^v \cdot \rho_{w,g} \quad (27)$$

in which:

$$J_{w,c,g} = \text{flux density of water vapour by convection of the gas phase} \\ (\text{kg m}^{-2}(\text{soil}) \text{ s}^{-1})$$

The convective dispersion of water vapour in the gas phase, assumed to be similar to that for fumigant vapour, is given by:

$$J_{w,dis,g} = - D_{w,dis,g} \frac{\partial \rho_{w,g}}{\partial z} \quad (28)$$

in which:

$$J_{w,dis,g} = \text{flux density of water vapour by dispersion in the gas phase} \\ (\text{kg m}^{-2}(\text{soil}) \text{ s}^{-1})$$

$$D_{w,dis,g} = \text{coefficient of convective dispersion of water vapour in the gas phase} \\ (\text{m}^3(\text{gas}) \text{ m}^{-1}(\text{soil}) \text{ s}^{-1})$$

The conservation equation for water in a soil system due to transport by diffusion, convection and dispersion in the gas phase is obtained by inserting the above mentioned flux densities in Equation (17):

$$\left[\frac{\partial c_w}{\partial t} \right]_{\text{dif+con,g}} = - \frac{\partial J_{w,dif,g}}{\partial z} - \frac{\partial J_{w,c,g}}{\partial z} - \frac{\partial J_{w,dis,g}}{\partial z} \quad (29)$$

8 CONVECTIVE TRANSPORT IN THE LIQUID PHASE

8.1 Flow of the liquid phase

Flow of the liquid phase is induced by water infiltrating the soil due to rainfall or irrigation or by evaporation of water at the soil surface. The flow of liquid through the soil in a one-dimensional system can be described by Darcy's Law (Koorevaar et al., 1983):

$$J_1^v = - \frac{K_1}{\rho_1} \frac{\partial p_h}{\partial z} \quad (30)$$

in which:

$$\begin{aligned} J_1^v &= \text{volume flux density of liquid flow} && (\text{m}^3(\text{liquid}) \text{ m}^{-2}(\text{soil}) \text{ s}^{-1}) \\ K_1 &= \text{hydraulic conductivity of the soil} && (\text{kg}(\text{liquid}) \text{ m}^{-1}(\text{soil}) \text{ Pa}^{-1} \text{ s}^{-1}) \\ \rho_1 &= \text{density of liquid phase} && (\text{kg}(\text{liquid}) \text{ m}^{-3}(\text{liquid})) \\ p_h &= \text{hydraulic pressure} && (\text{Pa}) \end{aligned}$$

The soil moisture characteristic ($p_h - \Theta_1$ relationship) depends on the pore size distribution in the soil and on soil composition, such as the clay and organic matter contents. When describing the flow of water in a vertical direction, the hydraulic pressure p_h is composed of two terms: the tensiometer pressure and a term caused by gravity, i.e. gravitational pressure. Multiplying the hydraulic conductivity of the soil by the dynamic viscosity of water gives the intrinsic permeability of the soil, which depends only on its pore geometry. Values for the intrinsic permeability of several soil types forming stable porous media, have been given in Section 7.1.

Flow of water under a temperature gradient has been discussed by Ten Berge (1986). He derived that such a gradient is not a substantial driving force, so this effect is neglected in the present discussion on water flow.

The final conservation equation for transport of water through the soil system (without plant growth) is obtained by inserting the flux density of liquid flow in Equation (29):

$$\frac{\partial c_w}{\partial t} = - \frac{\partial J_{w,dif,g}}{\partial z} - \frac{\partial J_{w,c,g}}{\partial z} - \frac{\partial J_{w,dis,g}}{\partial z} - \frac{\rho_l \cdot \partial J_1^v}{\partial z} \quad (31)$$

Models for water flow have been presented by e.g. Ten Berge (1986), Boesten (1986), Feddes et al. (1988), and Wagenet et al. (1989). When flow of soil liquid occurs, the contribution of water vapour transport to the total water transport is small, because of the large difference in density of liquid water versus water vapour. However, the transport of water vapour may substantially influence the soil moisture profile in the absence of liquid flow.

8.2 Convection of fumigant

When flow of liquid through the soil system occurs, the fraction of fumigant present in the liquid phase is transported along with it. The transport of fumigant by convective transport with the liquid phase is described by:

$$J_{f,c,l} = J_l^v \cdot C_l \quad (32)$$

in which:

$$J_{f,c,l} = \text{flux density of fumigant by convection of the liquid phase} \\ (\text{mol m}^{-2}(\text{soil}) \text{ s}^{-1})$$

Similar to the variation of flow velocity of the gas phase in the soil system, the flow velocity of the liquid phase varies with the diameter of the pores and also within the pores. These differences will result in an increased spreading of fumigant through the soil. The transport of fumigant by convective dispersion in the liquid phase is described as:

$$J_{f,dis,l} = - D_{f,dis,l} \frac{\partial C_l}{\partial z} \quad (33)$$

in which:

$$J_{f,dis,l} = \text{flux density of fumigant by dispersion in the liquid phase} \\ (\text{mol m}^{-2}(\text{soil}) \text{ s}^{-1})$$

$$D_{f,dis,l} = \text{coefficient of convective dispersion of fumigant in the liquid phase} \\ (\text{m}^3(\text{liquid}) \text{ m}^{-1}(\text{soil}) \text{ s}^{-1})$$

Assuming the dispersion coefficient to be proportional to J_l^v (Boesten, 1986), it follows that:

$$D_{f,dis,l} = L_{f,dis,l} \cdot |J_l^v| \quad (34)$$

in which:

$$L_{f,dis,l} = \text{dispersion length for convection of fumigant in the liquid phase} \\ (\text{m}(\text{soil}))$$

The complete conservation equation for fumigant in soil is obtained by inserting the divergence of the flux densities of fumigant by convection and dispersion with the liquid phase in Equation (26):

$$\frac{\partial C_s}{\partial t} = - \frac{\partial J_{f,dif,g}}{\partial z} - \frac{\partial J_{f,dif,l}}{\partial z} - \frac{\partial J_{f,c,g}}{\partial z} - \frac{\partial J_{f,dis,g}}{\partial z} - \frac{\partial J_{f,c,l}}{\partial z} - \frac{\partial J_{f,dis,l}}{\partial z} \\ + R_{fo} - R_{ur} \quad (35)$$

To assess the effect of convective dispersion of fumigant in the liquid phase versus diffusion of fumigant through the liquid and gas phases, values of the Péclet number need to be calculated (See Section 7.2). When comparing the convective dispersion of fumigant in the liquid phase with the diffusion of fumigant in the liquid phase, the Péclet number equals the volume flux density of liquid flow, J_1^V , multiplied by the dispersion length, $L_{f,dif,l}$, and divided by the actual coefficient of diffusion of fumigant in the liquid phase, $D_{f,dif,l}$. When comparing the convective dispersion of fumigant in the liquid phase with the diffusion of fumigant in the gas phase, the above mentioned product of volume flux density and dispersion length must be multiplied by K_{lg} and divided by the actual coefficient of diffusion of fumigant in the gas phase, $D_{f,dif,g}$. As an example, transport of (Z)-1,3-dichloropropene is considered to occur in a homogeneous soil system at a temperature of 15 °C with volume fractions of the liquid and gas phases of 0.3 and 0.2, respectively. In the Netherlands, hourly volume flux densities of rainfall of about $1.2 \cdot 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$ (100 mm d^{-1}) occur frequently (Boesten, 1986). The dispersion length for convective dispersion through the liquid phase was taken to be 0.01 m, which corresponds to the intermediate value for this parameter in the study by Boesten (1986) on the transport of herbicides through the soil. The coefficient of diffusion of (Z)-1,3-dichloropropene in air and water is taken to be $8.1 \cdot 10^{-6}$ and $8.1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. The actual coefficients for the diffusion of (Z)-1,3-dichloropropene through the gas and liquid phases in the soil system are then calculated to be $2.8 \cdot 10^{-7}$ and $4.9 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$, respectively. At 15 °C, the value of K_{lg} of (Z)-1,3-dichloropropene is 21. The values for the Péclet number when comparing the effect of convective dispersion in the liquid phase versus diffusion in the gas and liquid phases in this example are calculated to be 0.9 and 250, respectively. From these values it is evident that with flow of liquid through the soil, convective dispersion of fumigant in the liquid phase is more important to its spreading in soil than diffusion in the liquid phase. The contribution of convective dispersion in the liquid phase is of the same order of magnitude as that of diffusion in the gas phase. However, a higher value for the dispersion length than that used in the present example results in a greater contribution of convective dispersion of fumigant in the liquid phase to its transport in soil.

The contribution of the transport of fumigant by convection with the liquid phase versus that of the transport of fumigant by diffusion through the gas phase can be estimated from the values of the corresponding fluxes. Assuming the concentration of (Z)-1,3-dichloropropene decreases from C_g to zero over a distance of 0.1 m, the flux density of diffusion through the gas phase is equal to $10 \cdot D_{f,dif,g} \cdot C_g$. At 15 °C, the value for the coefficient of diffusion of (Z)-1,3-dichloropropene in a soil system with a volume fraction of the gas phase of 0.2 is calculated to be $2.8 \cdot 10^{-7} \text{ m}^2 \text{ s}^{-1}$. At equilibrium at 15 °C, the average concentration of this fumigant in the liquid phase of the 0.1 m thick layer is equal to $0.5 \cdot K_{lg} \cdot C_g$, the K_{lg} at this temperature being 21. The average flux density of (Z)-1,3-dichloropropene by convection of the liquid phase is then $0.5 \cdot K_{lg} \cdot C_g \cdot J_1^V$. For one hour with a volume flux density of liquid flow of $1.2 \cdot 10^{-6} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1}$, the ratio between the flux density of fumigant by convection of the liquid phase and the flux density of fumigant by diffusion through the gas phase equals about 5, which implies that both processes are then important for the transport of fumigant. It should be noted that

a higher concentration gradient than that used in the present example occurs shortly after injection, resulting in a change in the ratio as calculated above in favour of diffusion through the gas phase. In the course of time, the concentration gradients of fumigant in the gas phase decrease, thereby decreasing the contribution of diffusion to the total transport of fumigant compared with that by convection with the liquid phase.

To estimate the contribution by convective transport of fumigant with the liquid phase versus that by convection with the gas phase, the ratio for the partitioning of (Z)-1,3-dichloropropene between the liquid and gas phases can be used as an indicator. For rainwater infiltrating the soil, the absolute magnitude of the volume flux of gas phase by convection can be expected to approach that of the volume flux of liquid phase by convection (volume fluxes with opposite sign). As the concentration of (Z)-1,3-dichloropropene in the liquid phase at 15 °C is about 20 times higher than that in the gas phase, convective transport of fumigant with the gas phase due to rainfall will be comparatively small.

When simulating fumigant behaviour in well-aerated soils of medium and fine texture, under conditions with little or no rainfall and evaporation, the transport of fumigant by diffusion through the gas phase dominates its spreading through the soil. Under such conditions, the transport of fumigant in soil can be described by considering only its diffusion in the gas phase. However, the transport of fumigant by convection with the liquid phase gains in importance as the volume flux density of rainfall increases, so during periods of substantial rainfall, its contribution needs to be included in the simulation model.

9 HEAT TRANSFER IN SOIL

9.1 Heat balance at the soil surface

The earth receives energy from the incoming solar radiation, but a fraction of this energy is lost through reflection by clouds and the soil surface. The net radiation flux at the soil surface consists of the net shortwave solar radiation plus the difference between the incoming longwave radiation from the atmosphere and the outgoing longwave radiation from the earth's surface. Heat is transferred through the soil away from or towards the soil surface. Temperature differences between the soil and the air flowing over it also result in a loss or gain of heat. A latent heat flux is caused by evaporation or condensation of water at the soil surface. Thus, the heat balance at the soil surface can be described by:

$$R_n + G + H_s + H_l = 0 \quad (36)$$

in which:

| | |
|--|------------------------------------|
| R_n = net solar radiation flux density | $(J\ m^{-2}(\text{soil})\ s^{-1})$ |
| G = soil heat flux density | $(J\ m^{-2}(\text{soil})\ s^{-1})$ |
| H_s = sensible heat flux density | $(J\ m^{-2}(\text{soil})\ s^{-1})$ |
| H_l = latent heat flux density | $(J\ m^{-2}(\text{soil})\ s^{-1})$ |

The net radiation flux density depends on soil moisture content and temperature. Also, it is affected significantly by the soil cover. The soil heat flux density depends on the thermal properties of the soil and this term is comparatively small compared with the other fluxes of the energy budget at the soil surface, in particular during the day (Van Ulden and Holtslag, 1985). The sensible and latent heat flux densities depend on temperatures and humidities in the air and at the soil surface, on wind speed and on surface roughness. The terms that constitute the energy budget have been discussed in detail by Holtslag and Van Ulden (1983), Van Ulden and Holtslag (1985) and Ten Berge (1986), and methods were presented to calculate the different surface heat flux densities.

9.2 Heat transfer in soil

Heat transfer through the soil occurs as a result of temperature differences. The transfer of heat by conduction depends on the temperature gradient and the conductivity of the soil for heat transfer. The one-dimensional transfer of heat through the soil by conduction in the vertical direction can be described by:

$$J_{h,c} = -\lambda \frac{\partial T}{\partial z} \quad (37)$$

in which:

$J_{h,c}$ = flux density of heat by conduction

(J m⁻²(soil) s⁻¹)

a = thermal conductivity

(J m⁻¹(soil) s⁻¹ K⁻¹)

The course of the soil temperature with depth and time depends on the thermal properties of the soil: the thermal conductivity and the volumetric heat capacity. The volumetric heat capacity is defined as the amount of energy needed to increase the temperature of a unit volume of soil by one Kelvin. The contributions of the soil components to the volumetric heat capacity as well as to the thermal conductivity vary widely (Van Wijk and De Vries, 1963b). The thermal conductivities of quartz, water and dry air at 20 °C are 8.5, 0.60, and 0.03 J m⁻¹ s⁻¹ K⁻¹, respectively. The volumetric heat capacities of quartz, water and dry air at 20 °C are 2 000, 4 200 and 1.2 kJ m⁻³ K⁻¹, respectively. Hence, changes in soil moisture content strongly influence the volumetric heat capacity and heat conductivity of the soil. Moreover, thermal conductivity is affected by the shape and arrangement of soil particles. Thus, it is not possible to predict these parameters for a particular soil without knowledge of its components and corresponding volume fractions as well as of the distribution of soil particles of different sizes and shapes. Calculation procedures to obtain estimates for the volumetric heat capacity and the thermal conductivity have been given by De Vries (1963).

Because the volumetric heat capacity of water is comparatively high, infiltration of water into a soil layer with a temperature different from that of the liquid distinctly affects the temperature of that layer. The heat flux density due to liquid transport can be described by:

$$J_{h,l} = J_l^v \cdot Q_{v,l} \cdot T \quad (38)$$

in which:

$J_{h,l}$ = heat flux density by transport of liquid

(J m⁻²(soil) s⁻¹)

$Q_{v,l}$ = volumetric heat capacity of liquid

(J m⁻³(liquid) K⁻¹)

Although the general impact of this flux density on the soil temperature profile is comparatively small (Ten Berge, 1986), rainwater with a temperature different from that of the soil surface layer may have a significant influence on the temperature profile in that layer.

The temperature profile of a soil may be influenced by thermal convection of soil air, in particular when a reversed temperature gradient occurs by cooling at the soil surface during the night and early morning (Ten Berge, 1986). On the other hand, in the description by Cohen et al. (1988) for the transport of soil air by thermal convection in a nearly dry loam soil it was assumed that such transport did not alter the soil temperature profile. The effect of thermal convection of moist air on the soil temperature profile can be expected to be greater due to the latent heat of condensation contained in water vapour.

The conservation equation for heat in soil can be given as:

$$\frac{\partial Q_s \cdot T}{\partial t} = - \frac{\partial J_{h,c}}{\partial z} - \frac{\partial J_{h,l}}{\partial z} - \Delta H_{w,v} \frac{\partial J_{w,g}}{\partial z} + P_h - S_h \quad (39)$$

in which:

| | | |
|------------------|--|--|
| Q_s | = volumetric heat capacity of the soil | $(J \text{ m}^{-3}(\text{soil}) \text{ K}^{-1})$ |
| $\Delta H_{w,v}$ | = enthalpy of vaporization of water | $(J \text{ kg}^{-1})$ |
| $J_{w,g}$ | = total flux density of water vapour | $(\text{kg m}^{-2}(\text{soil}) \text{ s}^{-1})$ |
| P_h | = rate of heat production | $(J \text{ m}^{-3}(\text{soil}) \text{ s}^{-1})$ |
| S_h | = rate of heat consumption | $(J \text{ m}^{-3}(\text{soil}) \text{ s}^{-1})$ |

The terms P_h and S_h represent possible other sources or sinks of heat. Heat is produced with the adsorption of liquid water on dry soil. The release of heat upon the adsorption of liquid water occurs when the relative humidity of the soil air is below 0.2 (Ten Berge, 1986). Such low humidities are not likely to occur in the soil. Therefore, it is not included in the present description of the soil temperature profile. Various chemical and biological reactions occur in soil, which may be exothermic or endothermic.

Assuming no intermolecular interactions, the molar enthalpy for the formation of methyl isothiocyanate from metham-sodium could be estimated from the enthalpies of the bonds broken and those formed (Waser, 1966). At 25 °C and 101 kPa, the molar enthalpy for the formation of methyl isothiocyanate is calculated to be -13 kJ mol⁻¹. At an application rate of 300 L ha⁻¹, the amount of metham-sodium applied per square metre is 0.118 mol. The transformation of this amount would result in a release of 1.5 kJ and could increase the temperature in a soil layer 0.01 m thick by about 0.1 K (see Section 2.2). For the transformation of 1,3-dichloropropene into its main transformation product, 3-chloroallyl alcohol, a similar calculation can be made. This reaction is calculated to be slightly endothermic, the enthalpy being 6 kJ mol⁻¹. Because there is a gradual transformation of metham-sodium and 1,3-dichloropropene, the actual change in soil temperature can be expected to be much lower than 0.1 K. Thus, taking the amounts of fumigant applied to the soil into account, there is no need to include the related production or consumption of heat in the description of the course of the temperature with depth and time.

For pesticides with lower vapour pressures than those of the fumigants, models have been presented which include the effect of temperature on transport. Padilla and Lafrance (1988) presented a model for the transport of atrazine under non-isothermal conditions. In their description, they accounted for heat transfer by conduction and by transport of the liquid phase as well as for heat production and heat consumption. As the temperature difference between the soil surface and groundwater level was kept constant, no description was needed for the course of the temperature with time at the soil surface. Consequently, the effect of a diurnal change in soil temperature on atrazine transport could not be assessed.

9.3 Empirical description of soil temperatures

An empirical way to describe soil temperature as a function of depth and time has been presented by Van Wijk and De Vries (1963b). For a homogeneous soil, the relation to describe the soil temperature with position and time is given by:

$$\phi(z,t) = \phi_s + \Delta\phi_0 \exp(-z \cdot d^{-1}) \sin(f \cdot t - z \cdot d^{-1}) \quad (40)$$

in which:

$\phi(z,t)$ = temperature of the soil at depth z and time t (K)

ϕ_s = average soil temperature (K)

$\Delta\phi_0$ = amplitude of temperature at the soil surface (K)

d = damping depth (m(soil))

f = radial frequency of the temperature variation (rad s⁻¹)

The amplitude of the temperature fluctuation at depth z will be lower than at the soil surface. This can be explained by the storage or release of heat in soil layers with changes in temperature. Also, the diurnal amplitude will be higher at a bare soil surface than at a surface covered by grass. At the damping depth, the temperature amplitude is e^{-1} times the amplitude at the surface. In common soil types the diurnal variation is negligible below a depth of 0.5 m (Van Wijk and De Vries, 1963b). It should be noted that effects of weather factors such as rainfall and cloud cover on the soil temperature profile are not accounted for in Equation (40). However, Equation (40) can be used to estimate the order of magnitude of the effect of a diurnal change in soil temperature on processes such as fumigant diffusion through the gas-filled pore system. It has been used in the model described by Cohen et al. (1988) to assess the nature of the effect of diurnal changes in soil temperature on the behaviour of lindane in nearly dry loam soils.

10 GENERAL DISCUSSION AND CONCLUSIONS

After injecting liquid 1,3-dichloropropene into the soil, partitioning of this fumigant over the soil phases occurs by dissolution into the aqueous phase, adsorption onto the solid phase and vaporization into the gas phase of the soil system. The capacity of the aqueous phase to retain fumigant is much higher than that of the gas phase, so at equilibrium only a small fraction of fumigant will be present in the gas phase. The establishment of equilibrium for the partitioning of fumigant between the soil phases takes some time, so an assumption of instantaneous equilibrium is not always correct. Data on the kinetics of the transfer of fumigant across the soil liquid-liquid fumigant interface, of the adsorption of fumigant onto the solid phase, and of the partitioning of fumigant between the liquid and gas phases would give some information on the rate at which an equilibrium distribution of fumigant between the soil phases is established. Such information could be used to indicate under which conditions equilibrium in the partitioning of fumigant over the soil phases can be assumed to be instantaneous.

Measurements on the rate of transformation of fumigant in soil indicate that its description as a process with first-order kinetics is likely to be too simple. The rate at which the fumigant is transformed was found to be dependent on its initial concentration in soil. Comparatively high concentrations of fumigant in soil seem to inhibit microbial activity and consequently the rate at which the fumigant is transformed. However, part of the microbial population may adapt as a result of the (prolonged) presence of fumigant in soil, which may result in transformation of the fumigant at an enhanced rate. So far it has not been possible to predict whether or when such an enhancement will occur. Therefore, when using a simulation model for fumigant behaviour in soil, differences between the computed amounts of fumigant remaining in the soil and those measured can be expected.

Transport of fumigant through the soil under isothermal conditions, when there is little flow of the aqueous phase, occurs mainly by diffusion through the gas-filled pore system. Because of the large difference in magnitude between the coefficients for the diffusion of fumigant through the gas and liquid phases of the soil system, the contribution of liquid-phase diffusion to the transport of fumigant across greater distances through the soil can be neglected.

Thermal convection of soil air may occur when the temperature increases with the depth in soil; the influence of this process on the transport of fumigant through the gas-phase may be significant in dry soils of coarse texture or in loosely-tilled soils. Whether thermal convection occurs depends on factors such as the temperature gradient in soil and the soil physical properties. Temperature gradients resulting from a diurnal cycle will be smaller in moist soils than in dry soils, due to the much higher volumetric heat capacity of water compared with that of air. Therefore, less contribution of thermal convection to fumigant transport is expected in moist soils than in dry soils.

When flow of the liquid phase occurs, the transport of fumigant along with the liquid phase is an important term in the description of fumigant behaviour. Downward flow of liquid is induced by rainwater infiltrating the soil, whereas upward flow of liquid is induced by the evaporation of water at the soil surface. In the course of the autumn, the volume flux density of evaporation of water at the soil surface decreases, which results in an increase in the net downward transport of liquid. Further, as soil temperature decreases in the course of the autumn, the transformation of fumigant will proceed at a slower rate. Consequently, a larger fraction of fumigant may penetrate into deeper soil layers and eventually reach the groundwater. Therefore, the timing of fumigation can be expected to be an important factor in the policy to avoid contamination of groundwater.

The coefficient for the diffusion of fumigant through the gas phase is determined by the volume fraction of the gas phase and the tortuosity factor. In many descriptions of gas-phase diffusive transport, the coefficients are calculated using an empirical relation between the tortuosity factor and the volume fraction of the gas-phase. Possibly, not all air-filled pores are interconnected, so the actual volume of the gas phase available for the transport of fumigant by diffusion may be less than the total gas-filled fraction of the soil. In that case, the coefficient of diffusion as calculated from the volume fraction of the gas phase and the tortuosity coefficient may be an overestimation.

The empirical relation between the tortuosity factor and the volume fraction of the gas-phase may not hold in soils with heterogeneities in soil structure, such as alternating wetter and drier parts of the soil, large voids, and cracks. Such heterogeneities in soil structure may result in preferential transport of fumigant through the gas phase. Using a computer-simulation model, Leistra (1972) demonstrated the effect of local differences in soil density and the effect of cracks at the soil surface on the diffusion of 1,3-dichloropropene in soil after injection. Differences in soil density within the plough layer may be caused by the preparation of the plough layer shortly before injection, the pulling of the injector blades through the soil and by the pressing of the soil surface with a roller after injection. Further, remnants of the previous crop in the plough layer may also contribute to heterogeneities in the soil structure. Few data have been published in the literature on the effect of such heterogeneities on the actual diffusion of vapours through the gas-filled pore system. For an assessment of their effect, data on the relation between the number and geometry of the gas-filled pores in the plough layer and the coefficient of diffusion are needed for a range of volume fractions of the gas phase. Such data could be used to develop a method to estimate the actual coefficient of diffusion through the gas phase for heterogeneous soil layers. Measurements of this coefficient will be needed to check the estimation method.

Rainwater infiltrating the soil and evaporation of water at the soil surface affect the behaviour of fumigant in the soil in different ways. The flow of liquid caused by rainfall and evaporation results in the convective transport of fumigant along with it. Further, flow of liquid can be expected to result in the flow of soil air in the opposite direction and consequently in the convective transport of fumigant in the gas phase. Flow of liquid is likely to result in changes in the volume fractions of

the gas and liquid phases. This results in a change in the fractions of fumigant in these phases as well as in a change in the coefficients of diffusion of fumigant in the gas and liquid phases. Thus, changes in the soil moisture content affect the contributions of various processes and factors to the total flux density of fumigant through the soil.

In models presented so far for fumigant behaviour in soil, the processes are often considered to occur under isothermal conditions (Leistra, 1972; Siebering and Leistra, 1979; Mignard and Benet, 1989; Wagenet et al., 1989). However, various processes are strongly affected by temperature, such as the partitioning of fumigant between the liquid and gas phases and the rate coefficient for the transformation of fumigant. Therefore, the spread and persistence of fumigant in soil can be expected to be affected by diurnal changes in soil temperature. Such changes are most pronounced in the plough layer of the soil, which is also the layer into which the fumigant is injected. The course of the soil temperature profile with time depends on the energy balance at the soil surface, which is strongly influenced by weather conditions. Consequently, a description of the course of the soil temperature profile with time would require a temporal description of the flux densities determining this balance as well as a description of the transfer of heat through the soil.

The description of the spreading of fumigant in soil under non-isothermal conditions is complicated by the relations between the transport of liquid and water vapour and the transfer of heat. As the thermal properties of the soil depend on the moisture content, substantial changes in these properties can be expected as a result of rainwater infiltrating the soil or water evaporating at the soil surface. Because of this dependence, diurnal changes in temperature are smaller in wet soils than in dry ones. Further, as a result of the latent heat of water vapour, transport of water vapour within the soil may affect its temperature profile. Latent heat is lost to the atmosphere when water evaporates at the soil surface. As various important parameters in the description of the spreading of fumigant through the soil depend on temperature, for example the ratio for the partitioning of fumigant between the liquid and gas phases, the interdependence between water transport and heat transfer cannot be neglected when there are significant changes in the soil moisture content profile with time. This interdependence makes the simulation of fumigant behaviour in a non-isothermal system a complex task.

In the description of fumigant transport along with the liquid phase, equilibrium for the partitioning of fumigant over the soil phases was assumed to be instantaneous. However, in certain soils, a fraction of the adsorption sites may be less accessible to adsorbate molecules and temporary non-equilibrium may persist before diffusion of fumigant from the bulk solution to the adsorption sites results in an equilibrium partitioning of fumigant. Moreover, the presence of denser and looser structures in the soil may result in the flow of liquid containing fumigant through preferential channels, resulting in a greater spread of fumigant than in a soil with a homogeneous structure. Several authors have dealt with modelling non-equilibrium processes involving a stagnant phase (Van Genuchten & Wieringa, 1976; Bolt, 1979). Effects of non-uniform liquid flow on transport of methomyl and diazinon in greenhouse soil, as caused by heterogeneities in the soil structure, have been studied by Leistra

(1985). His computations showed a significant effect of irregular water flow on the amount of pesticide leached. Southworth et al. (1987) studied the transport of chlorobenzenes through soil containing a single artificial macropore and found that transport of these chemicals could not be described if preferential flow channels were not taken into account. Therefore, when describing the transport of fumigants in soil by convection with the liquid phase, attention should be paid to the occurrence and the size characteristics of heterogeneities in the soil structure.

The study of the behaviour of pesticides in soil using computer-simulation models has become an important tool for evaluating environmental consequences of pesticide use. A comprehensive model would need to take account of many processes and factors. The relevance of these processes and factors when describing fumigant behaviour depend to a large extent on the actual field conditions. Comprehensive models are not yet available and in the model descriptions to date a series of simplifying assumptions has been made due to a lack of data on parameters of relevant processes or due to difficulties encountered in the description of these processes. Whether certain simplifications are justifiable depends on the weather and soil conditions, so caution is needed when simplifications are introduced. To check the results obtained with a model, measurements on fumigant behaviour under different field conditions are needed. Then, by including more factors and processes, an assessment can be made of the impact and correctness of simplifications in the description of fumigant behaviour. Such studies would provide information on the conditions under which certain simplifications in the description of fumigant behaviour are justifiable. Finally, a validated model could be used to predict fumigant behaviour in situations of interest where no measurements are available.

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LIST OF SYMBOLS

| | | |
|-----------------|--|---|
| a | = thermal conductivity | (J m ⁻¹ (soil) s ⁻¹ K ⁻¹) |
| c _w | = water concentration in the soil system | (kg m ⁻³ (soil)) |
| d | = damping depth | (m(soil)) |
| f | = radial frequency of the temperature variation | (rad s ⁻¹) |
| k _{fo} | = rate coefficient of formation of fumigant | (s ⁻¹) |
| k _{tr} | = rate coefficient of transformation of fumigant | (s ⁻¹) |
| p | = pressure in gas phase | (Pa) |
| p _{fs} | = saturated vapour pressure of fumigant | (Pa) |
| p _h | = hydraulic pressure | (Pa) |
| p _o | = osmotic pressure | (Pa) |
| p _t | = tensiometer pressure | (Pa) |
| p _w | = actual water vapour pressure | (Pa) |
| p _{ws} | = saturated water vapour pressure | (Pa) |
| t | = time | (s) |
| w | = soil water content | (kg (liquid))/(kg (solid)) |
| z | = depth in soil | (m(soil)) |

| | | |
|----------------------|---|---|
| A | = coefficient | (s ⁻¹) |
| B | = exponential coefficient | (dimensionless) |
| C _g | = concentration of fumigant in the gas phase | (mol m ⁻³ (gas)) |
| C _l | = concentration of fumigant in the liquid phase | (mol m ⁻³ (liquid)) |
| C _s | = concentration of fumigant in soil system | (mol m ⁻³ (soil)) |
| C _{p,s} | = concentration of precursor in soil system | (mol m ⁻³ (soil)) |
| D _{A,dif,B} | = coefficient of diffusion of vapour A in gas B | (m ² (gas) s ⁻¹) |
| D _{f,dif,a} | = coefficient of diffusion of fumigant in air | (m ² (gas) s ⁻¹) |
| D _{f,dif,g} | = coefficient of diffusion of fumigant in the gas phase | (m ³ (gas) m ⁻¹ (soil) s ⁻¹) |
| D _{f,dif,l} | = coefficient of diffusion of fumigant in the liquid phase | (m ³ (liquid) m ⁻¹ (soil) s ⁻¹) |
| D _{f,dif,w} | = coefficient of diffusion of fumigant in water | (m ² (liquid) s ⁻¹) |
| D _{f,dis,g} | = coefficient of convective dispersion of fumigant in the gas phase | (m ³ (gas) m ⁻¹ (soil) s ⁻¹) |
| D _{f,dis,l} | = coefficient of convective dispersion of fumigant in the liquid phase | (m ³ (liquid) m ⁻¹ (soil) s ⁻¹) |
| D _{w,dif,g} | = coefficient of diffusion of water vapour in the gas phase | (m ³ (gas) m ⁻¹ (soil) s ⁻¹) |
| D _{w,dis,g} | = coefficient of convective dispersion of water vapour in the gas phase | (m ³ (gas) m ⁻¹ (soil) s ⁻¹) |
| F _{As} | = mol fraction of saturated vapour A in the gas-vapour mixture | (dimensionless) |
| G | = soil heat flux density | (J m ⁻² (soil) s ⁻¹) |
| H _l | = latent heat flux density | (J m ⁻² (soil) s ⁻¹) |
| H _s | = sensible heat flux density | (J m ⁻² (soil) s ⁻¹) |
| ΔH _a | = molar enthalpy of adsorption of fumigant on the solid phase | (J mol ⁻¹) |
| ΔH _d | = molar enthalpy of dissolution | (J mol ⁻¹) |

| | | |
|------------------|--|---|
| $\Delta H_{f,v}$ | = molar enthalpy of vaporization of fumigant | (J mol ⁻¹) |
| $\Delta H_{w,v}$ | = enthalpy of vaporization of water | (J kg ⁻¹) |
| J_v^v | = volume flux density of gas flow | (m ³ (gas) m ⁻² (soil) s ⁻¹) |
| J_l^v | = volume flux density of liquid flow | (m ³ (liquid) m ⁻² (soil) s ⁻¹) |
| $J_{f,c,g}$ | = flux density of fumigant by convection of the gas phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{f,c,l}$ | = flux density of fumigant by convection of the liquid phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{f,dif,g}$ | = flux density of fumigant by diffusion through the gas phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{f,dif,l}$ | = flux density of fumigant by diffusion through the liquid phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{f,dis,g}$ | = flux density of fumigant by dispersion in the gas phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{f,dis,l}$ | = flux density of fumigant by dispersion in the liquid phase | (mol m ⁻² (soil) s ⁻¹) |
| $J_{h,c}$ | = flux density of heat by conduction | (J m ⁻² (soil) s ⁻¹) |
| $J_{h,l}$ | = heat flux density by transport of liquid | (J m ⁻² (soil) s ⁻¹) |
| $J_{w,c,g}$ | = flux density of water vapour by convection of the gas phase | (kg m ⁻² (soil) s ⁻¹) |
| $J_{w,dif,g}$ | = flux density of water vapour by diffusion through the gas phase | (kg m ⁻² (soil) s ⁻¹) |
| $J_{w,dis,g}$ | = flux density of water vapour by dispersion in the gas phase | (kg m ⁻² (soil) s ⁻¹) |
| $J_{w,g}$ | = total flux density of water vapour | (kg m ⁻² (soil) s ⁻¹) |
| K_s | = air conductivity of the soil | (m ³ (gas) m ⁻¹ (soil) Pa ⁻¹ s ⁻¹) |
| K_l | = hydraulic conductivity of the soil | (kg(liquid) m ⁻¹ (soil) Pa ⁻¹ s ⁻¹) |
| $K_{l/g}$ | = ratio for the partitioning of fumigant between liquid and gas phases | (mol m ³ (liquid))/(mol m ³ (gas)) |
| $K_{s/l}$ | = ratio for the partitioning of fumigant between solid and liquid phases | (mol kg ⁻¹ (solid))/(mol m ³ (liquid)) |
| M | = molecular mass | (kg mol ⁻¹) |
| $L_{f,dis,g}$ | = dispersion length for convection of fumigant in the gas phase | (m(soil)) |
| $L_{f,dis,l}$ | = dispersion length for convection of fumigant in the liquid phase | (m(soil)) |
| P_h | = rate of heat production | (J m ⁻³ (soil) s ⁻¹) |
| Q_s | = volumetric heat capacity of the soil | (J m ⁻³ (soil) K ⁻¹) |
| $Q_{v,l}$ | = volumetric heat capacity of liquid | (J m ⁻³ (liquid) K ⁻¹) |
| R | = molar gas constant | (J mol ⁻¹ K ⁻¹) |
| R_{fo} | = rate of formation of fumigant | (mol m ⁻³ (soil) s ⁻¹) |
| R_n | = net solar radiation flux density | (J m ⁻² (soil) s ⁻¹) |
| R_{tr} | = rate of transformation of fumigant | (mol m ⁻³ (soil) s ⁻¹) |
| S | = surface area of vaporization | (m ² (gas)) |
| S_c | = solubility | (mol mol ⁻¹ (solvent)) |
| S_h | = rate of heat consumption | (J m ⁻³ (soil) s ⁻¹) |
| T | = temperature | (K) |
| T_0 | = reference temperature | (K) |
| V_A | = volume of vapour A formed | (m ³ (gas)) |

X = amount of fumigant adsorbed per unit mass of soil (mol kg⁻¹ (solid))

$\phi(z,t)$ = temperature of the soil at depth z and time t (K)

ϕ_a = average soil temperature (K)

$A\phi_0$ = amplitude of temperature at the soil surface (K)

ρ_l = density of liquid phase (kg(liquid) m⁻³(liquid))

$\rho_{w,g}$ = density of water vapour in the gas phase (kg m⁻³(gas))

$\rho_{w,l}$ = density of liquid water (kg m⁻³(liquid))

τ_g = tortuosity factor for diffusion in the gas phase (m²(soil) m⁻²(gas))

τ_l = tortuosity factor for diffusion in the liquid phase (m²(soil) m⁻²(liquid))

Γ = coefficient (K⁻¹)

Φ = coefficient (dimensionless)

Θ_g = volume fraction of the gas phase (m³(gas) m⁻³(soil))

Θ_l = volume fraction of the liquid phase (m³(liquid) m⁻³(soil))

**3 MODELLING THE EMISSION OF THE FUMIGANTS 1,3-DICHLORO-
PROPENE AND METHYL ISOTHIOCYANATE FROM SOIL TO AIR**
Report of DLO The Winand Staring Centre (SC-DLO Report 64)

ABSTRACT

Berg, F. van den and M. Leistra, 1992. *Modelling the emission of the fumigants 1,3-dichloropropene and methyl isothiocyanate from soil to air*. Wageningen (The Netherlands), DLO The Winand Staring Centre. Report 64. 81 pp.; 34 Figs; 13 Tables; 34 Refs.

After their injection into the soil, a fraction of the fumigants 1,3-dichloropropene and methyl isothiocyanate (formed from metham-sodium) diffuses up to the soil surface and escapes into the air. The rates of emission of the fumigants into the air were computed with a model describing their behaviour in soil. For both fumigants, it was computed that up to a few tens of percent of the dosage can be lost by volatilization. Deviations between the contents of methyl isothiocyanate measured in soil and those computed prompted further model development. A model for the behaviour of non-volatile pesticides in soil was extended and modified to estimate the effect of rainfall and evaporation and that of diurnal changes in soil temperature on the rate of emission of fumigant into the air.

Keywords: 1,3-dichloropropene, metham-sodium, methyl isothiocyanate, fumigants, nematocides, pesticides, fumigation, soil, modelling, emission, air
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Project 7245

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SUMMARY

In the Netherlands, the large-scale use of soil fumigants in agriculture has become a matter of concern in recent years. The fumigants 1,3-dichloropropene and metham-sodium (precursor of methyl isothiocyanate) are used to control soil-borne pathogens in arable farming. They are usually injected into the soil at a depth of between 0.15 and 0.20 m. After injection, a fraction of the fumigant diffuses up to the soil surface and escapes into the air. For an assessment of the rate and extent of fumigant emission into the air, a study was needed on the behaviour of fumigant in soil.

The rate of transformation of 1,3-dichloropropene was measured for the soil from two fields (afterwards injected with this fumigant). In an initial period ranging from 11 to 14 days, transformation kinetics was approximately first-order. Thereafter, the transformation accelerated and in about four days less than 2% of the dosage remained. The rate of transformation of methyl isothiocyanate was measured for the soil from two fields (afterwards injected with metham-sodium). In one soil, an initial period of 18 days with first-order kinetics was followed by a period with accelerated transformation. Within a few days less than 0.4% of the dosage remained. In the second soil, transformation kinetics remained approximately first-order.

A standard computation model was set up to describe the behaviour of fumigant in soil after injection. For the spreading of fumigant in soil, only diffusion through the gas phase was considered. The transformation of fumigant was assumed to follow first-order kinetics. Soil moisture condition and temperature were assumed to be constant. This model was used to simulate the two fields injected with 1,3-dichloropropene and the two other fields injected with metham-sodium. Input data for the model were obtained from measurements and from the literature.

During the first day after injection of 1,3-dichloropropene into the soil, the computed rate of emission into the air was comparatively low. Thereafter, a distinct increase in the rate of emission was computed. The computed maximum rate of emission of (Z)-1,3-dichloropropene was $62 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 11 for one field and $178 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 6 for the other field. The corresponding maxima computed for the less volatile (E)-isomer were $24 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 18 and $68 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 9, respectively. It was calculated that during the first three weeks following injection, the cumulative emissions were 9.5 and 22% of the dosage for the (Z)-isomer. They were 3.7 and 12% of the dosage for the (E)-isomer.

The computed rate of emission of methyl isothiocyanate into the air was comparatively low during the first day after the injection of metham-sodium. Thereafter, there was a distinct increase in the computed rate of emission. The computed maximum rates of emission of methyl isothiocyanate were $134 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 6 for one field and $251 \text{ mg m}^{-2} \text{ d}^{-1}$ on day 4 for the other field. For the first three weeks following the application of metham-sodium, the computed cumulative emissions of methyl isothiocyanate into the air were 19% and 27%, respectively, of the equivalent dosage (corresponding to the dosage of metham-sodium).

The computed spreading of fumigants in soil was checked on a limited scale with measurements in the field. The measured upward movement of 1,3-dichloropropene in one soil tended to be greater than that computed, but in the other soil this difference was not clear. Because of the higher volatility of the (Z)-isomer, there was more spreading of the (Z)-isomer than of the (E)-isomer. Little movement of 1,3-dichloropropene to depths around 0.3 m was computed and the same was found in the measurements.

Around the injection depth, the computed contents of methyl isothiocyanate tended to be higher than those measured in the soil of one field, but they tended to be lower in the soil of the other field. For both fields, a greater diffusion of methyl isothiocyanate to the soil surface was computed than was measured. In the soil of one field, the computed downward diffusion was greater than that measured, but in the soil of the other field there was little diffusion to depths below 0.3 m, both in the computations and the measurements.

The deviations between the computed spread of methyl isothiocyanate in soil and that measured in the field indicated that transformation kinetics in the soil was more complex than assumed. A content-dependent rate coefficient for the transformation of methyl isothiocyanate, as derived from laboratory studies, was introduced into the model. The spread in soil computed with the modified model corresponded more favourably to that measured in the field. The computed maximum rates of emission of methyl isothiocyanate were 83 and 116 $\text{mg m}^{-2} \text{d}^{-1}$ and they occurred at 6 and 3 days, respectively, after the injection of metham-sodium. The computations with this modified model resulted in a substantially lower cumulative emission than computed earlier. The newly computed emissions were 11 and 9.9%, respectively.

The effect of rainfall and water evaporation on the rate of emission of fumigant into the air was estimated by introducing a submodel for vapour diffusion in the gas phase into a model describing the behaviour of non-volatile pesticides in soil. Due to rainfall, the computed maximum rate of emission of (Z)-1,3-dichloropropene after injection into the soil of one field decreased from 178 to 125 $\text{mg m}^{-2} \text{d}^{-1}$. Accordingly, the cumulative loss of this fumigant by volatilization was computed to decrease substantially compared with the loss computed with the standard model. The cumulative loss in the first three weeks decreased from 22% to 16%.

The effect of diurnal changes in soil temperature on the rate of fumigant emission was estimated by further modifying the pesticide behaviour model by introducing a submodel describing the temperature at the soil surface and the transfer of heat in soil. Descriptions of the temperature-dependency of the rate coefficient of transformation and that of the ratios for the partitioning of fumigant between the soil phases were also introduced. For a diurnally changing soil temperature with an amplitude of 5 K, the computed rate of emission of fumigant into the air varied substantially during the day. At midday, the computed rate of emission was about 1.5 times higher than at midnight. However, the effect on cumulative fumigant volatilization in the first three weeks after injection was computed to be negligible.

1 INTRODUCTION

The effects of large-scale applications of pesticides in agriculture on the environment have become a major point of concern in recent years. In the discussions on the prolongation of their approval, possible environmental effects of pesticides will be evaluated in more detail than before. Adequate information is needed on the behaviour of pesticides in soil and on their emission into the other environmental compartments.

In the Netherlands, soil fumigants constitute an important group of agricultural pesticides, also in view of the amounts applied. Fumigants are used to prevent the development of large populations of soil-borne pathogens induced by intensive farming. In most instances, the fumigants are injected into the soil at a depth of between 0.15 and 0.20 m. The fumigant 1,3-dichloropropene is a volatile liquid, whereas metham-sodium is injected as an aqueous solution. Metham-sodium is transformed in the soil to the volatile and nematicidal methyl isothiocyanate. The vapour pressures of (Z)- and (E)-1,3-dichloropropene at 20 °C are 3.3 and 2.5 kPa, respectively (Goring, 1962). The vapour pressure of methyl isothiocyanate is lower: 1.7 kPa at 20 °C (Smelt and Leistra, 1974). A fraction of 1,3-dichloropropene and methyl isothiocyanate reaches the soil surface and escapes into the air (Leistra and Frissel, 1975; Siebering and Leistra, 1979). The rates of emission are needed as input values for the source strength in computations on the concentration patterns of the fumigants in the air around fumigated fields.

In computer-simulation models describing fumigant behaviour in soil, vapour diffusion in the gas phase is usually assumed to be the predominant transport process (Siebering and Leistra, 1979). They reported coefficients for the diffusion of 1,3-dichloropropene and methyl isothiocyanate in air, which were obtained using an estimation method described by Reid and Sherwood (1966), of 0.69 and 0.78 m² d⁻¹ at 20 °C, respectively. The diffusion coefficient of the fumigant in soil largely depends on the volume fraction of the gas-filled pore system. Consequently, changes in soil moisture content due to rainfall and evaporation affect this coefficient. Fluctuations in the coefficient of diffusion through the gas-filled pore system due to such changes will be most pronounced in the topsoil. The contribution of convective transport by flow of the gas phase in soil to the spread of fumigant may be important. In the computations of Wagenet et al. (1989), the enhancement of the coefficient of diffusion through the gas phase of the soil, as calculated for pressure fluctuations of 2.5 kPa with a frequency of 0.25 d⁻¹, was 0.13 m² d⁻¹.

Diffusion in the liquid phase is assumed to make only a minor contribution to the transport over greater distances in soil, but is essential for local equilibration of fumigant between the soil phases. Jury et al. (1983) calculated that for most pesticides the coefficient of diffusion in the gas phase is about four orders of magnitude higher than that in the liquid phase. Thus, it seems warranted to neglect the contribution of diffusion in the liquid phase to fumigant transport over greater distances in soil.

Fumigants are transformed in soil by microbial activity, but other processes may also make a contribution, such as hydrolysis in the soil solution (McCall, 1987) and reactions with soil constituents. Adequate description of transformation kinetics is essential for computer simulation of fumigant behaviour in soil. The rate of transformation of a fumigant is dependent on factors such as soil type, temperature and soil moisture condition. Recently, enhanced transformation of fumigants in soil, sometimes after an initial period with a more gradual transformation, was reported (Smelt et al., 1989a,b,c).

In this study, a standard computer-simulation model for the behaviour of fumigant in soil is used to calculate the rate of emission into the air under field conditions. The input data were derived from two fields treated with 1,3-dichloropropene and from two other fields treated with metham-sodium. The rate of transformation of the fumigants in the soil from these fields was measured. Other parameters (e.g. for the partitioning of fumigant between the soil phases) were collected from the literature. The rates of emission into the air are calculated for the first few weeks after injection of the fumigant into the soil.

The spread of fumigant in the topsoil of the four fumigated fields was measured on a limited scale. The differences between the contents of methyl isothiocyanate in soil measured and those computed indicate that the transformation of methyl isothiocyanate did not follow straightforward first-order kinetics. Therefore, a content-dependent rate coefficient is introduced into the model to check whether this improves the simulation of the behaviour of methyl isothiocyanate in soil. Further, the model for the behaviour of non-volatile pesticides in soil as developed by Boesten (1986) is extended and modified to include vapour diffusion through the gas phase, which enables the effect of rainfall and evaporation on the rate of emission of fumigant into the air to be estimated. Subsequently, the model is extended with a submodel for the variations of temperature at the soil surface and for the transfer of heat in the soil. Descriptions of the temperature-dependence of parameters sensitive to temperature changes are introduced into the model. This enables the effect of diurnal changes in soil temperature on the rate of emission of fumigant into the air to be estimated.

2 DESCRIPTION OF THE FIELD EXPERIMENTS

The four selected fields are located in the arable region in the northeast of the Netherlands. Fields DA, DB and MA are situated near Valthermond (Province of Drenthe) and field MB is situated near Eeserveen (also Province of Drenthe). Fields DA and DB cover an area of 5.1 (632 by 81 m) and 6.2 ha (759 by 82 m), respectively, and fields MA and MB cover an area of 6.1 (742 by 82 m) and 3.5 ha (331 by 105 m), respectively.

Fields DA and DB were injected with 150 litres 1,3-dichloropropene per hectare (applied as Telone II) at the end of October and the beginning of November 1987, respectively. The trade product Telone II contains more than 92% of a mixture of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene. The ratio between the (Z)-isomer and the (E)-isomer in this product is about 1.2. Fields MA and MB were injected with 300 litres of an aqueous metham-sodium solution (0.51 kg l^{-1}) per hectare in early October 1986 and at the end of September 1987. These are the dosages used in practice for nematode control in potatoes. The fumigants were injected using a horizontal-blade type injector with spray-nozzles under the blades. The fumigants were injected at a depth of between 0.15 and 0.20 m, after which the soil surface was compressed with a roller.

Shortly before injection of the fumigants, soil samples were taken from the top 0.2 m layer of the fields. These were used in incubation studies in the laboratory to measure the rate of transformation of fumigant in soil (Section 3). Some characteristics of the plough layer of the fields selected are presented in Table I.

Table I: Characteristics of the soil in the top 0.2 m layer of the fumigated fields (Laboratory for Soil and Crop Testing at Oosterbeek).

| Field | pH-KCl | Organic matter content (%) | Mineral fraction (%) | |
|-------|--------|----------------------------------|----------------------|--------------------|
| | | | <2 μm | 2-50 μm |
| DA | 5.1 | 15.7 | 2.7 | 7.3 |
| DB | 5.4 | 24.6 | 0.3 | 1.3 |
| MA | 4.3 | 13.8 | 2.5 | 7.2 |
| MB | 5.2 | 6.2 | 2.2 | 6.2 |

The volume fractions of the soil phases in the topsoil of the fields were calculated from measurements made for samples taken shortly after the application of the fumigant. The soil samples were taken with rings (volume 100 cm^3) at five sites per field. The samples were weighed before and after drying at 105°C for 24 hours. It was assumed that the densities of the mineral and organic constituents were 2 660

kg m^{-3} and $1\,470\text{ kg m}^{-3}$, respectively. The volume fraction of gas-filled pores was calculated from the volume fraction solid phase and the volume fraction liquid phase. The results are shown in Table II.

The comparatively small fractions of the solid phase in the soil of fields DA, DB and MA are due to their fairly high organic matter contents (see Table I). It should be noted that the decrease in bulk density with depth for the soil of field MA is due to an increase in the organic matter content.

The procedure and results of the incubation study for each fumigant as well as specifications on the analysis of each fumigant in soil are described in Section 3. The data on the fumigants to be used in the standard model are presented in Section 5. The introduction of these data and that of data on the conditions of the soil at the time of fumigation into the model are described in Section 6. Soil sampling to determine content profiles of the fumigants in the topsoil is described in Section 8.

Table II: Bulk densities and volume fractions of the phases in the topsoil of the fumigated fields.

| Field | Layer (m) | Bulk density (kg m ⁻³) | Volume fractions of phases | | |
|-------|--------------|---------------------------------------|----------------------------|-------|------|
| | | | solid | water | gas |
| DA | 0.00-0.05 | 730 | 0.31 | 0.37 | 0.32 |
| | 0.05-0.10 | 750 | 0.32 | 0.37 | 0.31 |
| | 0.10-0.15 | 770 | 0.33 | 0.39 | 0.28 |
| | 0.15-0.20 | 810 | 0.35 | 0.42 | 0.23 |
| | 0.20-0.25 | 810 | 0.37 | 0.47 | 0.16 |
| | 0.25-0.30 | 860 | 0.39 | 0.44 | 0.17 |
| | 0.30-0.35 | 720 | 0.33 | 0.47 | 0.20 |
| DB | 0.00-0.05 | 830 | 0.36 | 0.35 | 0.29 |
| | 0.05-0.10 | 820 | 0.36 | 0.38 | 0.26 |
| | 0.10-0.15 | 930 | 0.41 | 0.40 | 0.19 |
| | 0.15-0.20 | 900 | 0.39 | 0.46 | 0.15 |
| | 0.20-0.25 | 860 | 0.36 | 0.49 | 0.15 |
| | 0.25-0.30 | 740 | 0.31 | 0.58 | 0.11 |
| | 0.30-0.35 | 980 | 0.41 | 0.52 | 0.07 |
| MA | 0.00-0.05 | 650 | 0.28 | 0.18 | 0.54 |
| | 0.05-0.10 | 700 | 0.30 | 0.23 | 0.47 |
| | 0.10-0.15 | 690 | 0.30 | 0.23 | 0.47 |
| | 0.15-0.20 | 790 | 0.36 | 0.23 | 0.41 |
| | 0.20-0.25 | 710 | 0.30 | 0.29 | 0.41 |
| | 0.25-0.30 | 540 | 0.25 | 0.38 | 0.37 |
| | 0.30-0.35 | 230 | 0.14 | 0.48 | 0.37 |
| MB | 0.00-0.05 | 1 210 | 0.48 | 0.21 | 0.31 |
| | 0.05-0.10 | 1 180 | 0.47 | 0.20 | 0.33 |
| | 0.10-0.15 | 1 130 | 0.44 | 0.20 | 0.35 |
| | 0.15-0.20 | 1 250 | 0.49 | 0.20 | 0.31 |
| | 0.20-0.25 | 1 280 | 0.51 | 0.22 | 0.28 |
| | 0.25-0.30 | 1 330 | 0.53 | 0.26 | 0.21 |
| | 0.30-0.35 | 1 350 | 0.53 | 0.27 | 0.20 |

3 RATE OF TRANSFORMATION IN SOIL

3.1 Introduction

The rate of transformation of 1,3-dichloropropene in soil is influenced by soil characteristics and temperature. Smelt et al. (1989c) incubated 1,3-dichloropropene in six loamy soils at 15 °C, at initial contents of between 62 and 80 mg kg⁻¹. They measured a gradual transformation for a period of 3 to 6 days following application, but after that the transformation rate increased rapidly and no fumigant was detectable after about 7 days. The high rate of transformation was ascribed to microorganisms being adapted to 1,3-dichloropropene. Van der Pas and Leistra (1987) incubated 1,3-dichloropropene in three sandy soils also at 15 °C, at initial contents of 24 and 124 mg kg⁻¹. At the higher initial content for two of the three soils, an initial period with approximate first-order kinetics of about 26 days was followed by a stage with accelerated transformation. For the third soil, the initial period with a more gradual transformation was shorter: about 12 days. At the lower initial content, the rate of transformation for the three soils studied was high right from the beginning. The occurrence of accelerated transformation was also measured in two loamy soils under field conditions, after an initial period of 3 to 8 days after injection (Smelt et al., 1989b).

After being injected into the soil, metham-sodium is transformed into the volatile methyl isothiocyanate. Metham-sodium is stable in concentrated aqueous solutions, but is transformed upon dilution (Hartley and Kidd, 1987). In acidic media, the anionic form of metham-sodium can undergo transformation by the transfer of a proton from nitrogen to sulphur, which results in the formation of methyl isothiocyanate and sulphide (Joris et al., 1970). The transformation of metham-sodium to methyl isothiocyanate in aqueous solutions (distilled water or 0.01 N CaCl₂) is promoted by ions of heavy metals (Ashley and Leigh, 1963) and by soil particles (Gerstl et al., 1977). Smelt et al. (1989a) measured the transformation of metham-sodium in sandy and loamy soils at 15 °C and found that more than 90% of it was transformed to methyl isothiocyanate. The maximum amounts of methyl isothiocyanate were measured within 0.1 to 1.0 day after application.

The rate of transformation of the volatile methyl isothiocyanate varies with soil type. Smelt and Leistra (1974) measured half-lives of 9 to 14 days for sandy soils at 13 °C. The transformation rate of methyl isothiocyanate at 15 °C measured by Smelt et al. (1989a) in sandy and loamy soils differed considerably: time periods for 50% transformation ranged from 0.5 to 50 days. They found a high rate of transformation of this fumigant in several soils with a known history of treatments, which is possibly due to microbial adaptation. However, in some other soils no accelerated transformation was measured, even after several applications. Moreover, accelerated transformation of methyl isothiocyanate was also found in soils which had no history of treatments. The induction of accelerated transformation, as well as the time after application at which this acceleration starts, is difficult to predict. Repeated application of the same fumigant may induce accelerated transformation.

Incubation studies in the laboratory were needed to obtain data on the rate of transformation of the fumigants in the soil of the fields studied. Soil samples were collected from the plough layer of the four fields shortly before the fields were injected with 1,3-dichloropropene or metham-sodium. In the laboratory, known amounts of fumigant were added to soil samples in gas-tight glass flasks. Conditions in the laboratory experiments approximated those in the field at the time of fumigation.

3.2 Procedures

Approximately 25 samples per field were taken from the upper layer (0.0 - 0.2 m) and pooled per field. After mixing, subsamples of 100 g moist soil from fields DA, DB and MB were put into a series of 200 ml glass flasks, which were then closed with screw caps containing a rubber disc covered with aluminium foil. Similar subsamples from field MA were put into a series of 500 ml glass flasks with ground-glass stoppers (NS 46). The moisture content of the soils was adjusted to the average moisture content at the time of fumigation, i.e. 51%, 63%, 31% and 18% for the soil from fields DA, DB, MA and MB, respectively. The soil samples were pre-incubated for a period of two to six days prior to adding the fumigant.

For fields DA and DB incubations, a volume of 3.0 μl 1,3-dichloropropene (analytical grade; ratio of the (Z)- to the (E)-isomer about one) was added to each flask. For fields MA and MB incubations, solutions in water were prepared from methyl isothiocyanate (purity 99.8%). For field MA incubations, 0.7 ml of a 10 mg ml^{-1} solution was added to the soil in the flasks and for field MB incubations about 0.4 ml of a 5 mg ml^{-1} solution. As soon as the fumigant had been added, the flasks were closed and placed upside down in a water bath to obtain a gas-tight seal. The initial content of 1,3-dichloropropene in the soil was approximately 30 mg per kg dry soil for each of the isomers. The initial content of methyl isothiocyanate was approximately 100 and 30 mg per kg dry soil for the incubations with soil from fields MA and MB, respectively. The amounts of fumigant added to the flasks were checked by adding similar doses of fumigant to 100 ml of extraction solvent. The incubations for fields DA, DB and MA were done in the dark at 10 °C and those for field MB at 15 °C. These temperatures approximated the average temperatures in the plough layer at the time of fumigation.

At various times during a period of 21 days, soil batches incubated with 1,3-dichloropropene were extracted by shaking for 1.5 hours with 100 ml hexane and 50 ml water. The soil batches incubated with methyl isothiocyanate were extracted by shaking with 100 ml ethyl acetate and 50 ml water. After separation of the liquid layers, a fraction of the solvent layer was transferred into a glass tube with stopper and stored in a deep-freeze until analysis.

A volume of 2 μl of the 1,3-dichloropropene extracts was injected into a gas chromatograph (HP 5890) with CP 57 CB column (10 m long; 0.50 mm i.d.; Chrompack). The injection, column and detection temperatures for the measurements of 1,3-dichloropropene were 120, 70 and 300 °C, respectively. The flow rate of the

carrier gas (N_2) was about 10 ml min^{-1} . This fumigant was measured with an electron capture (EC) detector. The retention times for (Z)- and (E)-1,3-dichloropropene were 2.0 and 2.9 minutes, respectively. The concentrations in the extracts were calculated after measuring standard solutions of fumigant in hexane. The limit of determination for 1,3-dichloropropene was 0.1% of the dosage.

A volume of 3 μl of the methyl isothiocyanate extracts was injected into a gas chromatograph (Pye Unicam GCV) with glass column (1.4 m long, 4.0 mm i.d.) packed with 3% Carbowax 20 M on Chromosorb W AW-DMCS. The injection, column and detection temperatures were 150, 110 and 210 $^{\circ}\text{C}$, respectively. The flow rate of the carrier gas (N_2) was 60 ml min^{-1} . Methyl isothiocyanate was measured using a flame photometer detector operating in the sulphur mode at 394 nm. The retention time for methyl isothiocyanate was 1.0 min. The concentrations in the extracts were calculated after measuring standard solutions of this fumigant in ethyl acetate. The limit of determination for methyl isothiocyanate was either 0.7% of the dosage (for the field MA incubations) or 0.4% (for the field MB incubations).

3.3 Results

3.3.1 Transformation of 1,3-dichloropropene

The percentages of 1,3-dichloropropene remaining in the soil from field DA at various time intervals are presented in Figure 1. The transformation could roughly be described by first-order kinetics until about 40% was left after 11 days of incubation. After this initial period the transformation accelerated. After 16 and 18 days of incubation, the amounts of 1,3-dichloropropene were below 2% of the dosage and after 21 and 23 days they were below the determination limit, i.e. 0.1% of the dosage.

The percentages of 1,3-dichloropropene remaining in the soil from field DB at various time intervals are presented in Figure 2. The transformation could roughly be described by first-order kinetics until about 40% of the dosage was left after 14 days of incubation. Thereafter, the transformation accelerated. After 18 days of incubation, the amount of each isomer remaining was approximately 1% of the dosage and after 21, 23, and 24 days of incubation the amounts were below the determination limit.

For the initial periods with approximate first-order kinetics, the best-fitting lines were calculated for the percentage remaining (log-scale) against time, by linear regression using the method of least squares. The values for the transformation rate coefficients of 1,3-dichloropropene as calculated for the soil from fields DA and DB are presented in Table III. The corresponding half-lives ranged from 10 to 12 days, for both the (Z)-isomer and the (E)-isomer.

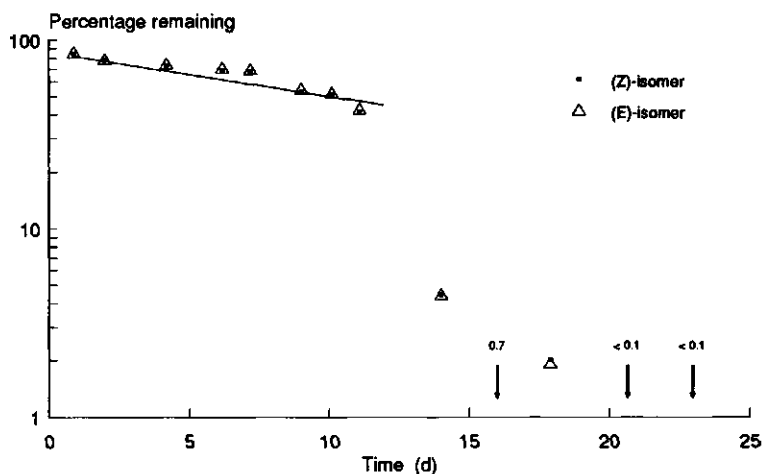


Fig. 1 Rate of transformation of 1,3-dichloropropene in soil of field DA, at 10 °C.

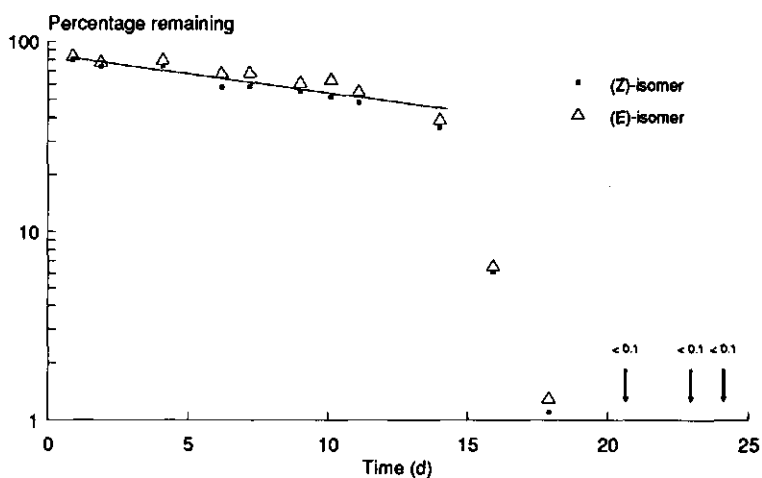


Fig. 2 Rate of transformation of 1,3-dichloropropene in soil of field DB, at 10 °C.

Table III: First-order rate coefficients, k , for the initial period of transformation of 1,3-dichloropropene in the soils of fields DA and DB. Incubation temperature 10 °C.

| Field | Period | k , (d ⁻¹) | |
|-------|--------------|--------------------------|------------|
| | | (Z)-isomer | (E)-isomer |
| DA | up to day 11 | 0.071 | 0.068 |
| DB | up to day 14 | 0.060 | 0.058 |

3.3.2 Transformation of methyl isothiocyanate

The percentages of the dosage of methyl isothiocyanate remaining in the soil from field MA at various time intervals are presented in Figure 3. In the whole incubation period of 21 days, the transformation could be approximated with first-order kinetics. After the incubation period of 21 days, 48% of the added amount of methyl isothiocyanate remained in the soil. No incubated soil samples were available to follow the transformation further.

The percentages of the dosage of methyl isothiocyanate remaining in the soil from field MB at various time intervals are presented in Figure 4. The transformation could be approximated with first-order kinetics up to 18 days of incubation. After this initial period, the transformation accelerated and the percentages of the dosage of methyl isothiocyanate remaining after 21, 23 and 24 days of incubation were below the determination limit, i.e. 0.4% of the dosage (corresponding to 0.1 mg kg⁻¹ (dry soil)).

Again, the best-fitting lines were calculated for the percentage remaining (log-scale) against time. The values for the first-order rate coefficient of transformation, k , of methyl isothiocyanate as calculated for the soil from fields MA and MB are presented in Table IV. The half-lives of this fumigant in the soil of fields MA and MB were 19 and 11 days, respectively.

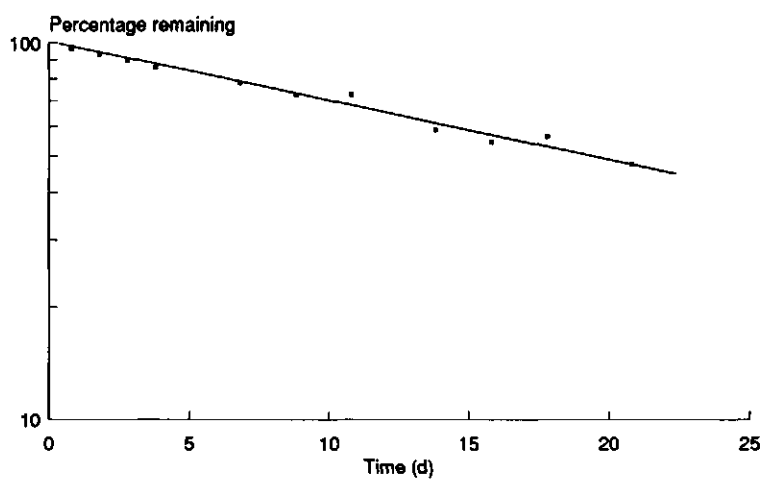


Fig. 3 Rate of transformation of methyl isothiocyanate in soil of field MA, at 10 °C.

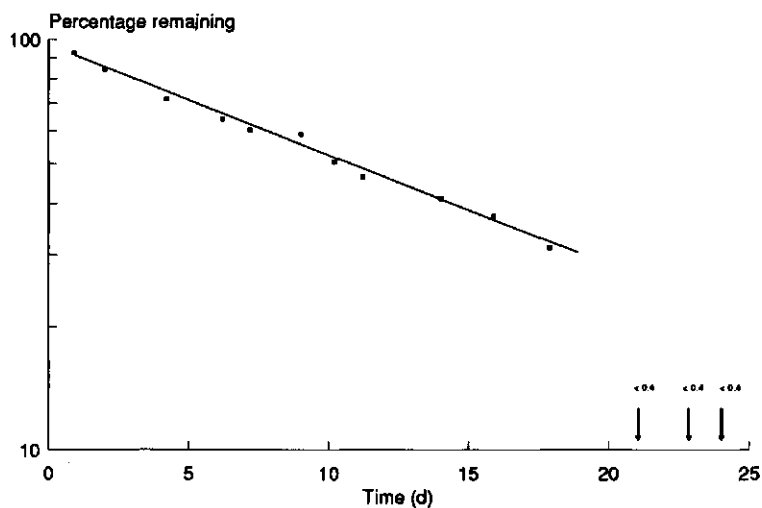


Fig. 4 Rate of transformation of methyl isothiocyanate in soil of field MB, at 15 °C.

Table IV: First-order rate coefficients, k_1 , for the initial period of transformation of methyl isothiocyanate in the soils of fields MA and MB.

| Field | Temperature (°C) | Period | k_1 (d ⁻¹) |
|-------|---------------------|--------------|-----------------------------|
| MA | 10 | up to day 21 | 0.036 |
| MB | 15 | up to day 18 | 0.062 |

3.4 Discussion

The incubations with 1,3-dichloropropene showed that for the soil from fields DA and DB the initial period with approximate first-order kinetics was 11 and 14 days, respectively. After a stage with accelerated transformation of about 4 days, less than 2% of the dosage remained. Presumably, soil organisms adapt their enzymes, so that the fumigant is transformed at a much higher rate. The course in the transformation of 1,3-dichloropropene with time as measured in the soil of fields DA and DB, i.e. accelerated transformation after an initial period with a more gradual transformation, is similar to that measured in loamy soils by Smelt et al. (1989c; see also Section 3.1).

It should be noted that the rate of transformation of 1,3-dichloropropene in soil as measured during the stage with approximate first-order kinetics is much higher than the rate of hydrolysis in aqueous solutions. For solutions of 1,3-dichloropropene at a pH ranging from 5 to 9 the half-life was measured to be 51 days at 10 °C (McCall, 1987). Smelt et al. (1989c) measured a half-life for 1,3-dichloropropene in distilled water at 10 °C of 51 days. The higher rate of transformation measured in soils compared with that in aqueous solutions may have been caused by catalysis of the transformation of 1,3-dichloropropene by soil components or by microbial activity (e.g. cometabolism).

The incubations with methyl isothiocyanate for the soil of fields MA and MB showed a transformation with approximate first-order kinetics during the first 21 and 18 days, respectively. After this initial period, transformation accelerated in the soil from field MB. No such accelerated transformation was measured for the soil from field MA. At the end of the 21-day incubation period for the soil of this field, about half the dosage still remained. The initial rate of transformation of methyl isothiocyanate in the soil of field MB corresponds with the range of values for the rate coefficient of transformation of this fumigant measured in sandy soils by Smelt and Leistra (1974; see also Section 3.1), i.e. from 0.05 to 0.08 d⁻¹. The lower rate measured for the soil from field MA may be explained by the lower temperature, i.e. 10 °C compared with that (15 °C) in the incubation experiment for the soil of field MB and that (13 °C) in the study of Smelt and Leistra (1974). The differences in starting contents of methyl isothiocyanate between the incubation series with soil of fields MA and MB,

i.e. 100 and 30 mg kg⁻¹, respectively, may also have contributed to this difference between the rate coefficients. Possibly, microbial activity was somewhat inhibited at the higher starting content of fumigant.

Methyl isothiocyanate is comparatively stable in aqueous solutions. Boesten et al. (1991) reported a 3% loss of methyl isothiocyanate in demineralized water during storage for 30 days at 13 °C. Ashley and Leigh (1963) measured the loss of methyl isothiocyanate at a concentration of 45 mg l⁻¹ in distilled water to be about 10% during storage for 24 days at room temperature, which corresponds to a half-life of about 160 days. There is little information in the literature on the transformation products of methyl isothiocyanate in aqueous solutions.

Ashley et al. (1963) measured the transformation of methyl isothiocyanate in soil (at 15 °C) in incubations using glass-stoppered bottles. The half-lives of methyl isothiocyanate in clay and peaty soils were about 11 and 4 days, respectively. After sterilizing the soil by heating, the half-lives were about 39 and 28 days, respectively. As sterilization did not fully inhibit the transformation of methyl isothiocyanate, the transformation as measured in these soils may have been due to a combination of microbial and chemical processes.

For both 1,3-dichloropropene and methyl isothiocyanate, the accelerated transformation following the period with transformation at a more gradual rate can be ascribed to microbial activity. The duration of the initial period or lag-phase is different (Smelt et al., 1989a,c). There are indications that microbial activity may be inhibited when contents of the fumigant are high (Smelt et al, 1989c). As the occurrence of enhanced transformation may easily result in insufficient nematode control in potato-growing, there is a need for further study on the causes of such enhancement and the factors influencing it.

4 DERIVATION OF EQUATIONS

The basic elements of a computer-simulation model for the behaviour of fumigant in soil have been described by Siebering and Leistra (1979). They used a differential equation in which terms are included for various processes, such as adsorption, gas-phase diffusion and transformation. Their approach is used as a point of departure in the derivation of the equations for the standard simulation model in this report.

As a result of its volatility, a fraction of the fumigant will be in the gas phase of the pore system. The ratio between the concentrations of fumigant in the liquid and gas phases can be described by:

$$C_l = K_{l/g} \cdot C_g \quad (1)$$

in which:

C_l = concentration in the liquid phase (kg m⁻³(liquid))

$K_{l/g}$ = ratio for the partitioning between the liquid and gas phases
((kg m⁻³(liquid))/(kg m⁻³(gas)))

C_g = concentration in the gas phase (kg m⁻³(gas))

It was calculated for 1,3-dichloropropene that the fraction of this fumigant present in the gas phase at temperatures of between 2 and 20 °C was less than 1% of the total mass per unit soil volume (Leistra, 1972). Because of the higher volatility of the (Z)-isomer, its fraction in the gas phase is somewhat higher than that of the (E)-isomer. Because of its lower volatility, the fraction of methyl isothiocyanate present in the gas phase may be lower than that of (E)-1,3-dichloropropene.

The most simple sorption model is based on the linear adsorption isotherm, which can be described as:

$$X = K_{s/l} \cdot C_l \quad (2)$$

in which:

X = amount adsorbed per unit mass of solid phase (kg kg⁻¹(solid))

$K_{s/l}$ = ratio for the partitioning between the solid and liquid phases
((kg kg⁻¹(solid))/(kg m⁻³(liquid)))

In a study on the adsorption of 1,3-dichloropropene on humic sand, Leistra (1972) concluded that a linear adsorption isotherm was adequate for concentrations of the (Z)-isomer in the gas phase ranging up to 0.033 kg m⁻³. Similar results were obtained for the (E)-isomer. The concentration range for which this linear relationship is valid is the most important one when considering adsorption under field conditions. In the temperature range from 2 to 20 °C, no deviation from this relationship was measured. In autumn, when many fumigations are done, the temperature in the topsoil is generally within this range. In the computations, a linear isotherm corresponding to Equation (2) was taken for the adsorption of 1,3-dichloropropene and methyl

isothiocyanate onto the solid phase. Further, it was assumed that local equilibrium existed between the concentrations of fumigant in the soil phases.

The concentration of fumigant in the soil system, C_s , can be described as:

$$C_s = \Theta_g \cdot C_g + \Theta_l \cdot C_l + \rho_b \cdot X \quad (3)$$

in which:

| | | |
|------------|---------------------------------------|--|
| C_s | = concentration in the soil system | (kg m ⁻³ (soil)) |
| Θ_g | = volume fraction of the gas phase | (m ³ (gas) m ⁻³ (soil)) |
| Θ_l | = volume fraction of the liquid phase | (m ³ (liquid) m ⁻³ (soil)) |
| ρ_b | = soil bulk density | (kg(solid) m ⁻³ (soil)) |

A fumigant capacity factor Q can now be defined:

$$Q = \Theta_g + \Theta_l \cdot K_{lg} + \rho_b \cdot K_{lg} \cdot K_{sl} \quad (4)$$

Combination of Equations (3) and (4) gives:

$$C_s = Q \cdot C_g \quad (5)$$

It is assumed that the ratios for the partitioning between the soil phases are constant within the soil profile and that the capacity factor does not vary with time. Isothermal soil conditions are assumed.

For many pesticide and soil combinations, the first-order type reaction is reported to describe transformation well (Boesten, 1986). This type of reaction is given by:

$$R_t = k_t \cdot C_s \quad (6)$$

in which:

| | | |
|-------|--------------------------------------|--|
| R_t | = rate of transformation | (kg m ⁻³ (soil) d ⁻¹) |
| k_t | = rate coefficient of transformation | (d ⁻¹) |

In the standard model it is assumed that transformation of fumigants can be described by first-order kinetics and that the rate coefficients are constant within the soil profile. No acceleration in the transformation rate of 1,3-dichloropropene and methyl isothiocyanate was taken into account.

In the standard model only transport by diffusion in the gas phase is considered. The diffusion flux density for the fumigant in the soil is described by:

$$J_{\text{dif},g} = -D_{\text{dif},g} \frac{\partial C_g}{\partial z} \quad (7)$$

in which:

| | | |
|--------------------|---|--|
| $J_{\text{dif},g}$ | = flux density by diffusion through gas phase | (kg m ⁻² (soil) d ⁻¹) |
|--------------------|---|--|

$$\begin{aligned} D_{\text{dif},g} &= \text{coefficient of diffusion in the gas phase} && (\text{m}^3(\text{gas}) \text{ m}^{-1}(\text{soil}) \text{ d}^{-1}) \\ z &= \text{depth in soil} && (\text{m}(\text{soil})) \end{aligned}$$

The coefficient for diffusion of fumigant in the gas phase of the soil system depends on the volume fraction of the gas phase. A further correction of this coefficient is needed because of the tortuosity of the soil pores. This relationship can be described by:

$$D_{\text{dif},g} = D_{\text{dif},a} \cdot \tau_g \cdot \Theta_g \quad (8)$$

in which:

$$\begin{aligned} D_{\text{dif},a} &= \text{coefficient of diffusion in air} && (\text{m}^2(\text{gas}) \text{ d}^{-1}) \\ \tau_g &= \text{tortuosity factor for diffusion in the gas phase} && (\text{m}^2(\text{soil}) \text{ m}^{-2}(\text{gas})) \end{aligned}$$

The tortuosity factor depends on the volume fraction of the gas phase. Experimental values for this coefficient have been compiled by Leistra (1972). Further, it is assumed that $D_{\text{dif},g}$ does not vary with time.

The mass conservation equation for the fumigant in the soil system is:

$$\frac{\partial C_s}{\partial t} = - \frac{\partial J_{\text{dif},g}}{\partial z} - R_t \quad (9)$$

in which:

$$t = \text{time} \quad (d)$$

To model the behaviour of methyl isothiocyanate in soil, a positive term R_t needs to be added to the right-hand side of Equation (9) to account for the formation of this fumigant from its precursor metham-sodium, which is the chemical injected into the soil.

In the numerical approach to this problem, the soil system is divided into computation compartments of thickness Δz . Such a method can cope with heterogeneities in the soil and changes in time (Leistra, 1986). Using the explicit finite-difference method with time interval Δt and changing over to the amount of fumigant (A) per compartment, the numerical solution of Equation (9) is given by (Siebering and Leistra, 1979):

$$\begin{aligned} \frac{(A_z^{t+\Delta t} - A_z^t)}{\Delta t} &= D_{\text{dif},g,z,z+\Delta z} \frac{(C_{g,z+\Delta z}^t - C_{g,z}^t)}{\Delta z} - D_{\text{dif},g,z,z-\Delta z} \frac{(C_{g,z}^t - C_{g,z-\Delta z}^t)}{\Delta z} \\ &\quad - k_t \cdot A_z^t \end{aligned} \quad (10)$$

The computational stability condition to be met for Equation (10) is:

$$\frac{D_{\text{diff.g}} \cdot \Delta t}{Q \cdot \Delta z^2} \leq 0.5 \quad (11)$$

The solution is obtained after programming in a suitable computer language; in this study CSMP III was used (Continuous System Modeling Program III; IBM, 1975).

5 INPUT DATA FOR THE STANDARD MODEL

5.1 Application of the fumigants

The starting amounts of (Z)- and (E)-1,3-dichloropropene for fields DA and DB were $8.99 \cdot 10^{-3}$ and $7.55 \cdot 10^{-3}$ kg m⁻², respectively. For fields MA and MB, the starting amount of metham-sodium was $1.53 \cdot 10^{-2}$ kg m⁻². The depths of injection for fields DA, MA and MB were taken to be 0.18 m, and that for field DB to be 0.16 m.

5.2 Rates of transformation

The transformation rate coefficient for metham-sodium was taken to be 12.0 d⁻¹. This value is based on a study of the transformation of metham-sodium in soils by Smelt and Leistra (1974). The efficiency of the transformation of metham-sodium to methyl isothiocyanate was taken to be 90 % (Smelt and Leistra, 1974), which results in a rate coefficient for the formation of methyl isothiocyanate of 10.8 d⁻¹.

Because the rate coefficient is dependent on temperature, the coefficients for 1,3-dichloropropene and methyl isothiocyanate as measured for each soil in the laboratory need to be adjusted to the average temperature in the plough layer during the period of fumigation. The following description for the dependence of the rate coefficient on temperature was suggested by Boesten (1986):

$$k_i(T) = k_i(T_0) \exp\{\Gamma(T - T_0)\} \quad (12)$$

in which:

T = temperature (K)

T₀ = reference temperature (K)

Γ = coefficient (K⁻¹)

Boesten (1986) showed that in the temperature range from 5 to 35 °C good approximations of the rate coefficient could be obtained using a value of Γ of 0.08 K⁻¹ (n = 54, s.d. = 0.02 K⁻¹). The transformation rate coefficients of 1,3-dichloropropene and methyl isothiocyanate corresponding to the average temperature in the plough layer during the period of fumigation were calculated from the coefficients obtained from the laboratory experiments using Equation (12), and with a value of 0.08 K⁻¹ for Γ. The values for 1,3-dichloropropene used in the computations are presented in Table V.

Table V: Estimated values for the rate coefficient of transformation, k_t , of 1,3-dichloropropene in soil at the average temperature in the plough layer of the fields in the fumigation period.

| Field | Temperature (°C) | k_t (d ⁻¹) | |
|-------|---------------------|--------------------------|------------|
| | | (Z)-isomer | (E)-isomer |
| DA | 9 | 0.066 | 0.063 |
| DB | 6 | 0.044 | 0.042 |

The transformation rate coefficients of methyl isothiocyanate as measured for the top 0.2 m layer of the fields MA and MB were also adjusted to correspond with the average temperature in the plough layer in the period of fumigation, i.e. 12 °C for field MA and 11 °C for field MB. The values for this coefficient used in the computations for fields MA and MB were 0.042 and 0.045 d⁻¹, respectively.

5.3 Physico-chemical characteristics of the fumigants

The values of the ratio for the partitioning of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene between the solid and liquid phases and for the partitioning between the liquid and gas phases for each soil were estimated for the average temperature in the plough layer in the fumigation period. They were derived from data presented by Leistra (1972) on the temperature-dependency of the ratios for the partitioning of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene between the organic matter and gas phases and that of the ratios for the partitioning of these isomers between the liquid and gas phases. Multiplying the ratio for the partitioning between the organic matter and gas phases by the fraction of organic matter in the plough layer of each field gives the ratio for the partitioning between the solid and gas phases for each soil. These values then need to be divided by the ratio for the partitioning between the liquid and gas phases to give those for the partitioning between the solid and liquid phases. The values used in the computations with the standard model are presented in Table VI.

Table VI: Estimated ratios for the partitioning between solid and liquid phase, K_{sl} , and for the partitioning between liquid and gas phase, K_{lg} , for 1,3-dichloropropene at the average temperature in the plough layer of the fields during fumigation (see Section 4, Equations (1) and (2)).

| Field | Temperature (°C) | K_{sl} (kg kg ⁻¹)/(kg m ⁻³) | | K_{lg} (kg m ⁻³)/(kg m ⁻³) | |
|-------|---------------------|--|----------------------|---|-----|
| | | | | | |
| | | (Z) | (E) | (Z) | (E) |
| DA | 9 | 2.3·10 ⁻³ | 2.6·10 ⁻³ | 34 | 53 |
| DB | 6 | 2.6·10 ⁻³ | 3.0·10 ⁻³ | 44 | 68 |

(Z) = (Z)-1,3-dichloropropene

(E) = (E)-1,3-dichloropropene

The values for the ratio of the partitioning of methyl isothiocyanate between the solid and liquid phases were calculated based on a study by Smelt and Leistra (1974). One of their experiments was done with a humic sandy soil at 12 °C. The value of the ratio for the partitioning of methyl isothiocyanate between the organic matter and liquid phases for that soil was used to obtain values of the ratio for the partitioning between the solid and liquid phases in the soil of the fumigated fields by multiplying it by the fraction of organic matter in the plough layer of those fields. The estimated ratios for the partitioning of methyl isothiocyanate between the solid and liquid phases, K_{sl} , at 12 °C for the soil of fields MA and MB were 0.5·10⁻³ and 0.2·10⁻³ (kg kg⁻¹)/(kg m⁻³), respectively. The values for the partition ratio between the liquid and gas phases were obtained by interpolating the partition ratios measured by Smelt and Leistra (1974) at different temperatures. The estimated values of K_{lg} at the temperatures in the plough layer of fields MA and MB during fumigation were 250 and 264 (kg m⁻³)/(kg m⁻³) at 12 and 11 °C, respectively.

Using an estimation method described by Reid and Sherwood (1966), the values for the diffusion coefficient of 1,3-dichloropropene in air at the average temperature in the plough layer of fields DA and DB were 0.64 (at 6 °C) and 0.66 m² d⁻¹ (at 9 °C). The diffusion coefficient of methyl isothiocyanate in air at the average plough layer temperature of fields MA (11 °C) and MB (12 °C) was estimated to be 0.73 m² d⁻¹. Values for the coefficient of diffusion in the gas-filled pore system were calculated using the data on the volume fractions of the gas phase of the soil of the fields studied (see Section 2, Table II) and the data on the tortuosity factor compiled by Leistra (1972).

6 STRUCTURE OF THE SIMULATION PROGRAM

The CSMP program contains an initial section and a dynamic section. The soil system is defined in the initial section. A soil profile with a depth of 0.5 m was considered. It was divided into 20 computation compartments, each $\Delta z = 0.025$ m thick. Taking the maximum value of $(D_{\text{diff}} \cdot \Delta)/(Q \cdot \Delta z^2)$ for the soil system into account, it was calculated that a time step of $\Delta t = 0.025$ d was adequate to meet the condition for computation stability.

Soil characteristics, such as bulk density and volume fractions of the gas and liquid phases were introduced in TABLE form as a function of depth (see Section 2, Table II). The dosages of 1,3-dichloropropene or metham-sodium were assigned to the compartment corresponding to the injection depth, being the 8th compartment from the top for fields DA, MA and MB and the 7th compartment from the top for field DB.

The bulk density and the volume fractions of the gas and liquid phases at the compartment centres were calculated by interpolating from the TABLES. Using these values, the fumigant capacity factor relative to the concentration in the gas phase was calculated for each compartment. The values for the volume fraction of the gas phase and the corresponding values for the tortuosity coefficient at the compartment boundaries were calculated by interpolating from TABLES. This enabled the diffusion coefficients of fumigant in the gas phase at the compartment boundaries to be calculated.

The transformation rate coefficient of metham-sodium and the formation rate coefficient of methyl isothiocyanate were introduced as parameters. The transformation rate coefficients and the partition ratios between the soil phases of 1,3-dichloropropene and methyl isothiocyanate were also introduced as parameters.

In the dynamic section of the program, first the rates of transformation of 1,3-dichloropropene or methyl isothiocyanate were calculated according to Equation (6). For methyl isothiocyanate as fumigant, this calculation was preceded by calculating the rate of transformation of metham-sodium and the rate of formation of methyl isothiocyanate. The rates of fumigant diffusion between the compartments were calculated using Equation (7). The lower boundary of the system was set at a depth of 0.5 m; hardly any diffusion to this depth occurred in the present conditions. Next, the rates of change in amount of fumigant per compartment were calculated and subsequently integrated over the time interval Δt . The resulting change in amount of fumigant over Δt was added to the amount at time t , to give the amount at time $t + \Delta t$ according to Equation (10). The situation at time $t + \Delta t$ was the starting point for a new cycle of computations.

Additional statements were introduced into the program to calculate the mass balance, the contents of the fumigant per compartment and the source strength of the emission to the atmosphere. The amount of metham-sodium transformed and the amount of

methyl isothiocyanate formed were calculated by integrating respectively the rate of transformation and the rate of formation, both over time. The total rate of transformation of 1,3-dichloropropene or methyl isothiocyanate was calculated by summing the rates per compartment, after which the rate was integrated over time, to give the total amount transformed. The total amount of fumigant remaining in the soil profile was calculated by summing the amounts in each soil compartment. The cumulative downward diffusion was calculated by integrating the diffusion flux at the lower boundary of the soil profile over time. The cumulative volatilization of the fumigant into the atmosphere was calculated by integrating the rate of diffusion at the soil surface. The content of the fumigant in each soil compartment was calculated (in mg kg^{-1}) to enable comparison with the contents measured in the fields.

7 COMPUTED EMISSION INTO THE AIR

7.1 Emission of 1,3-dichloropropene

The rates of emission of each isomer into the atmosphere computed for the fields studied are presented in Figures 5 and 6. For both fields, the rate of emission from the soil was computed to be comparatively low during the first day after injection of the fumigant. Thereafter, the computed rates increased more strongly. The maxima calculated for the rate of the emission of (Z)-1,3-dichloropropene were $62 \text{ mg m}^{-2} \text{ d}^{-1}$ for field DB on day 11 and $178 \text{ mg m}^{-2} \text{ d}^{-1}$ for field DA on day 6. The maxima calculated for (E)-1,3-dichloropropene were $24 \text{ mg m}^{-2} \text{ d}^{-1}$ for field DB on day 18 and $68 \text{ mg m}^{-2} \text{ d}^{-1}$ for field DA on day 9. The subsequent decrease in the computed rate of emission was more gradual. After three weeks the rates of emission were computed to be approximately $36 \text{ mg m}^{-2} \text{ d}^{-1}$ for the (Z)-isomer and $26 \text{ mg m}^{-2} \text{ d}^{-1}$ for the (E)-isomer.

Since transport of fumigant predominantly occurs through the gas phase, the rate of emission to the atmosphere is related to the concentration in the gas phase and to the volume fraction of that phase. The concentration in the gas phase is inversely proportional to the fumigant capacity factor. The average capacity factors for (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in soil from field DA were approximately 75 and $130 \text{ m}^3(\text{gas})/\text{m}^3(\text{soil})$, respectively. Higher average capacity factors for the (Z)- and the (E)-isomers were calculated for soil from field DB: 119 and $208 \text{ m}^3(\text{gas})/\text{m}^3(\text{soil})$, respectively. The comparatively low rate of the emission for field DB can be explained by the higher capacity factor.

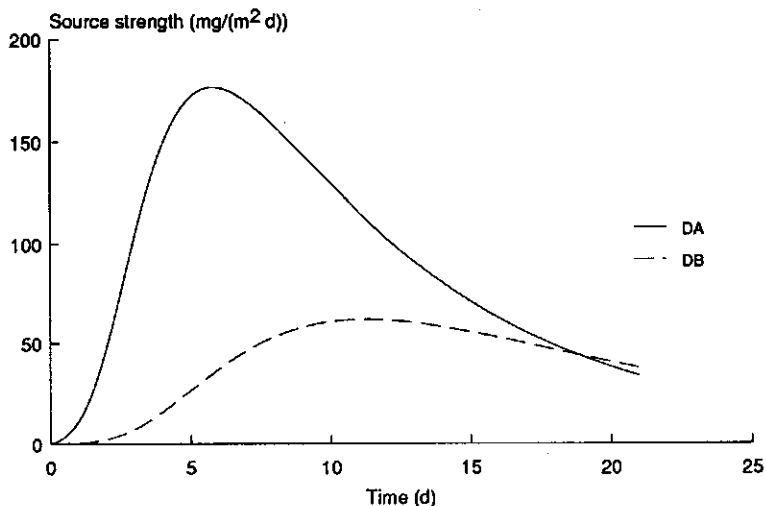


Fig. 5 Rate of emission of (Z)-1,3-dichloropropene from soil to air computed for fields DA and DB.

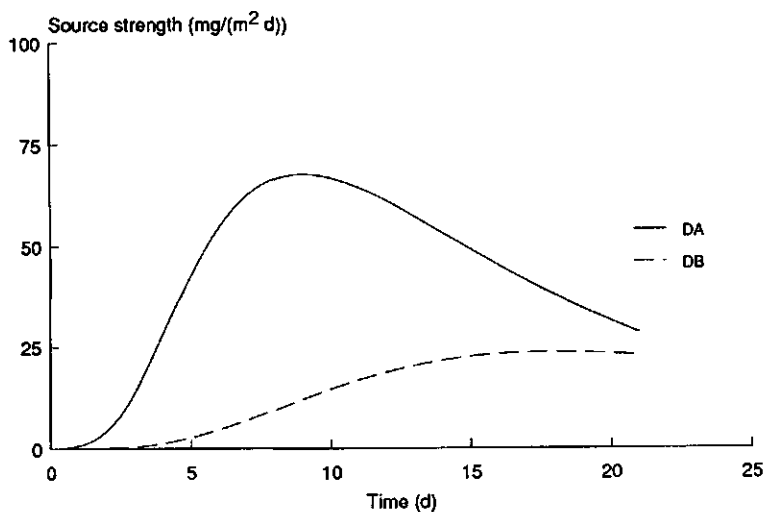


Fig. 6 *Rate of emission of (E)-1,3-dichloropropene from soil to air computed for fields DA and DB.*

The cumulative losses by volatilization at weekly intervals, expressed as a percentage of the dosage of each isomer, are presented in Tables VII and VIII.

Table VII: *Percentage of the dosage of (Z)-1,3-dichloropropene computed to be lost by volatilization from the soil of the fumigated fields.*

| Field | Cumulative volatilization (%) after | | |
|-------|-------------------------------------|---------|---------|
| | 1 week | 2 weeks | 3 weeks |
| DA | 8.3 | 18 | 22 |
| DB | 1.2 | 5.8 | 9.5 |

Table VIII: Percentage of the dosage of (E)-1,3-dichloropropene computed to be lost by volatilization from the soil of the fumigated fields.

| Field | Cumulative volatilization (%) after | | |
|-------|-------------------------------------|---------|---------|
| | 1 week | 2 weeks | 3 weeks |
| DA | 2.4 | 8.2 | 12 |
| DB | 0.2 | 1.6 | 3.7 |

For the period of the first three weeks after injection into the soil, a greater fraction of the (Z)-isomer was computed to be lost by volatilization than of the (E)-isomer, which is due to the somewhat higher volatility of the (Z)-isomer. During this period, the total loss of 1,3-dichloropropene by volatilization was computed to be 17% for field DA and 7% for field DB.

Albrecht and Chenchin (1985) measured concentrations of 1,3-dichloropropene in air at the soil surface after its injection into the soil at a depth of 0.45 m (dosage 293 l ha⁻¹). Soil temperature at injection depth was 26 °C and remained constant during the period in which the air samples were taken. For the first five days after injection, the concentration of 1,3-dichloropropene in air measured at the soil surface ranged from about 150 to 570 µg m⁻³. During the following weeks, the concentration in air at the surface decreased, until on day 30 it was below the detection limit, i.e. about 0.1 µg m⁻³. The concentrations in air measured at the soil surface indicate that already during the first day after injection, the rate of emission into the air was comparatively high. This is different from the emission pattern computed for the fields in the present study, which showed that the rate of emission increased more gradually after injection of 1,3-dichloropropene into the soil. Presumably, the much faster increase in the rate of emission from the field studied by Albrecht and Chenchin (1985) was the result of the much higher soil temperature, compared with that in the plough layer of the soils injected with 1,3-dichloropropene in our study: 26 °C versus 6 to 9 °C. Further, a higher soil temperature is expected to cause the maximum rate of emission of both isomers to occur at shorter time intervals after injection.

7.2 Emission of methyl isothiocyanate

The rates of emission of methyl isothiocyanate to the atmosphere computed for the fields studied are presented in Figure 7. Again, the rate of emission was computed to be comparatively low during the first day after injection of metham-sodium. After that, there was a stronger increase in the computed rate of emission. The maximum values calculated for the rate of emission of methyl isothiocyanate were 134 mg m⁻² d⁻¹ for field MB on day 6 and 251 mg m⁻² d⁻¹ for field MA on day 4. The subsequent

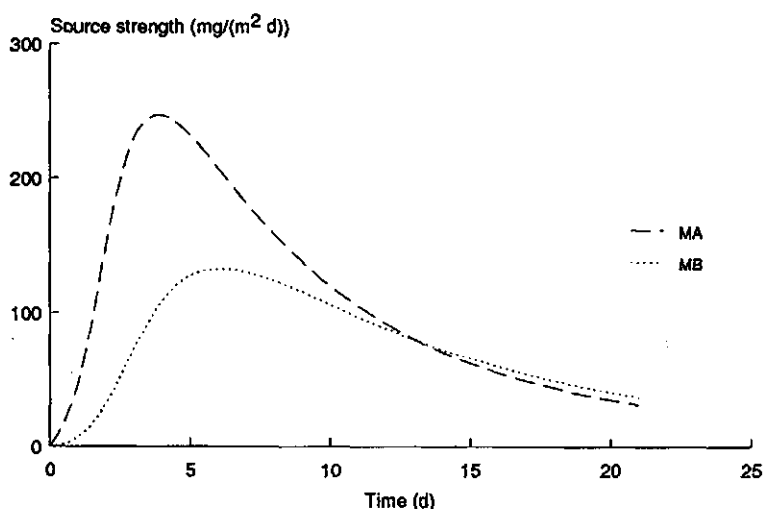


Fig. 7 Rate of emission of methyl isothiocyanate from soil to air computed for fields MA and MB.

decrease in the computed rate of emission was more gradual. Three weeks after injection of metham-sodium, the computed rate for field MA was at 13% of its maximum value and that for field MB at 28% of its maximum value.

The concentration of methyl isothiocyanate in the gas phase is inversely proportional to the fumigant capacity factor, so if only this factor is taken into account, the maximum rate of emission would be greater for field MB than for field MA. However, the maximum rate was computed to be higher for field MA. This can be explained by the lower volume fraction of the gas phase in the soil of field MB, which results in smaller values of the diffusion coefficient in the gas-filled pore system.

The cumulative loss by volatilization is expressed as a percentage of the equivalent dosage of methyl isothiocyanate corresponding to the actual dosage of its precursor metham-sodium. The values computed for this cumulative loss, at weekly intervals, are presented in Table IX. For the first three weeks after injection of metham-sodium, a substantial fraction of the dosage was computed to be lost by volatilization.

The emission patterns as computed are representative of sites of application where the fumigant is injected at a depth of between 0.15 and 0.20 m. Injection at other depths results in a different pattern of emission from the soil. Leistra and Crum (1990) simulated the behaviour of methyl isothiocyanate in greenhouse soil when metham-sodium was injected at a depth of between 0.10 and 0.15 m at a dosage of 1950 l ha⁻¹ (of a 0.51 kg l⁻¹ aqueous solution). The maximum rate of emission of methyl isothiocyanate was computed to be 39 500 mg m⁻² d⁻¹ at 0.5 d after injection of metham-sodium. This rate is much higher (hundredfold) than the maximum rates

Table IX: Percentage of the equivalent dosage of methyl isothiocyanate computed to be lost by volatilization from the soil of the fumigated fields.

| Field | Cumulative volatilization (%) after | | |
|-------|-------------------------------------|---------|---------|
| | 1 week | 2 weeks | 3 weeks |
| MA | 14 | 23 | 27 |
| MB | 6 | 15 | 19 |

computed for the fields in our study and occurred sooner after injection of metham-sodium. The difference can largely be explained by the higher application rate and the more shallow injection depth. As the injection depth decreases, less time is needed before the fumigant reaches the soil surface and the concurrent transformation will also be less, so higher diffusion flux densities will be reached at the soil surface. The decrease in the rate of emission from the greenhouse soil after it had reached its maximum was faster than that for the fields in this study: it decreased to 50% of its maximum in about one day.

8 CHECKS ON THE COMPUTED SPREADING IN SOIL

8.1 Introduction

The computations on the spreading of fumigants in soil using the standard model were checked by sampling and analysing different soil layers at a few time intervals after application of the fumigant. The content profiles of fumigant measured in the soil were compared with those computed with the model. It should be noted that the number of soil samples collected in the fields was very limited, so only trends can be given in the comparisons.

8.2 Procedures

The soil of fields DA and DB was sampled at four intervals after application of 1,3-dichloropropene. The soil of fields MA and MB was sampled at two time intervals after the application of metham-sodium. Each field was sampled at six sites to a depth of 0.35 m using a gouge auger. The soil core taken at each site was divided into sections of 0.05 m. Subsamples from the same layer were pooled in a flask containing 200 ml hexane (for 1,3-dichloropropene) or 200 ml ethyl acetate (for methyl isothiocyanate). In the laboratory, 100 ml water was added to each flask, which were then shaken for 1.5 hours. After the two liquid layers had separated, subsamples from the hexane or ethyl acetate layer were put into glass tubes with stoppers. The extracts were kept in a deep-freeze until analysis. The analytical procedures were as described before (see Section 3.2). The limit of determination of 1,3-dichloropropene in the soil samples was 0.1 mg kg^{-1} dry soil. The limit of determination of methyl isothiocyanate depended on the sampled mass of soil and ranged from 0.7 to 1.5 mg kg^{-1} dry soil.

8.3 Results

8.3.1 Content patterns of 1,3-dichloropropene

The contents of (Z)- and (E)-1,3-dichloropropene measured for field DA per layer of 0.05 m are presented in Figures 8 and 9, respectively. The highest contents of [(Z) plus (E)]-1,3-dichloropropene were measured around the injection depth, in the 0.15 - 0.20 m layer. As expected, lower contents of 1,3-dichloropropene were measured in the upper part of the soil profile, i.e. the 0.0 - 0.05 m and 0.05 - 0.10 m layers. During the first five days following the day of application, the contents measured in the 0.0 - 0.05 and 0.05 - 0.10 m layers increased, but subsequently decreased. For the period in which soil samples were taken, the contents measured below a depth of 0.3 m were less than 0.4 mg kg^{-1} .

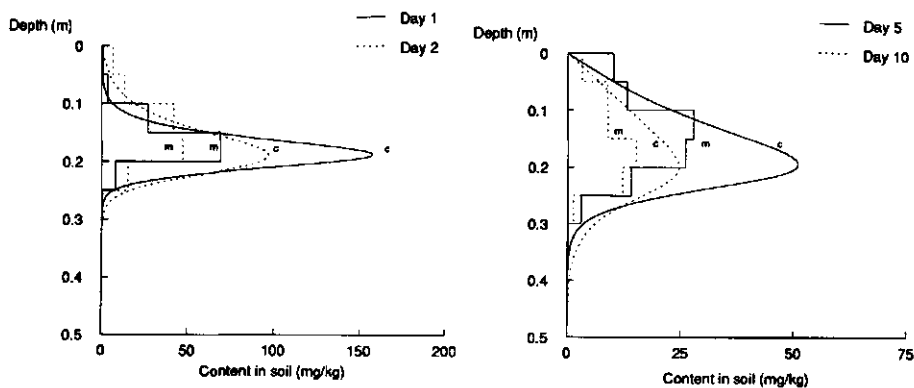


Fig. 8 Measured and simulated spread of (Z)-1,3-dichloropropene in the soil of field DA at four intervals after application. m=measured. c=calculated.

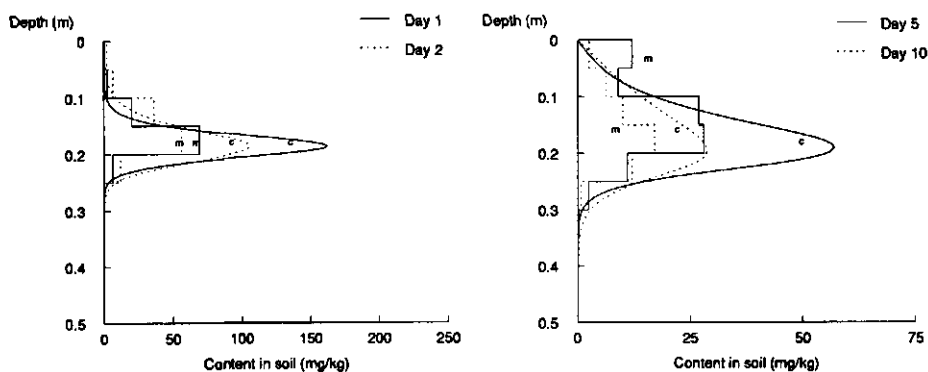


Fig. 9 Measured and simulated spread of (E)-1,3-dichloropropene in the soil of field DA at four intervals after application. m=measured. c=calculated.

Table X: Measured and computed contents of 1,3-dichloropropene in the 0.0 - 0.05 m layer of the soil of field DA.

| Days after injection | Content (mg kg ⁻¹) | |
|----------------------|--------------------------------|----------|
| | measured | computed |
| 1 | 1.1 | 0.1 |
| 2 | 8.6 | 1.9 |
| 5 | 22 | 7.2 |
| 10 | 5.6 | 6.6 |

Throughout the sampling period of ten days after the day of injection, the computed contents of [(Z) plus (E)]-1,3-dichloropropene for the 0.15 - 0.20 m layer were substantially higher than those measured in the field. The contents measured and computed for the 0.0 - 0.05 m layer are presented in Table X. During the first five days after injection, the computed contents of 1,3-dichloropropene in this layer were lower than those measured. On the tenth day after the day of application, the content calculated for the 0.0 - 0.05 m layer was slightly higher than that measured. For the first two days, the contents calculated for the layers below a depth of 0.30 m corresponded to the measurements in the field, but on the fifth and tenth days after the day of application, the contents computed for the 0.30 - 0.35 m layer were somewhat higher than those measured.

Data on the fate of 1,3-dichloropropene after injection into the soil of field DA are summarized in Figure 10. On the tenth day, 40% and 48% of the dosage of the (Z)- and (E)-1,3-dichloropropene, respectively, were calculated to remain. The percentages measured were lower: 22% and 26% of the dosages, respectively. It was calculated that 14% of the (Z)-isomer and 19% of the (E)-isomer would remain after a period of 21 days.

The contents of (Z)- and (E)-1,3-dichloropropene calculated and measured for field DB are represented in Figures 11 and 12, respectively. During the first nine days after the day of injection, the highest contents of [(Z) plus (E)]-1,3-dichloropropene were measured around the injection depth, which for this soil was close to 0.15 m. During this period, much lower contents were measured in the 0.0 - 0.05 m layer. On the sixth and ninth days, the contents measured in this layer were higher than those measured during the first three days. The contents measured below a depth of 0.3 m remained low throughout the whole period: they were less than 0.3 mg kg⁻¹.

On the first day after the day of application, the highest content of [(Z) plus (E)]-1,3-dichloropropene was calculated for the 0.15 - 0.20 m layer, whereas in the field the highest content was measured in the 0.10 - 0.15 m layer. When the average

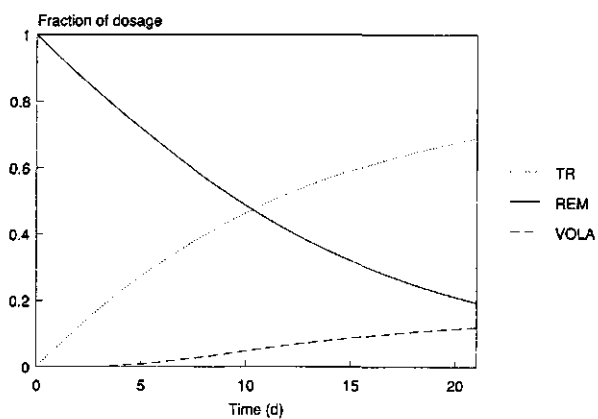
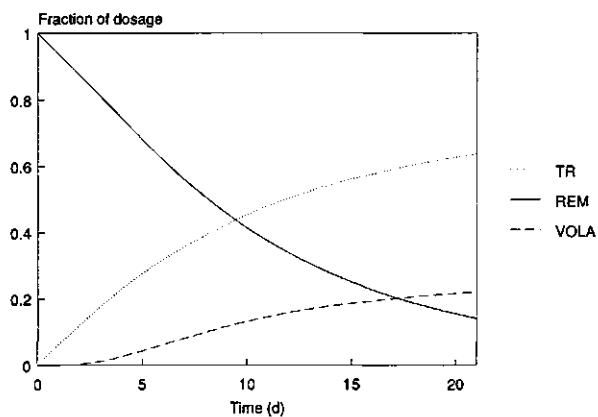


Fig. 10 Simulated fate of (Z)-1,3-dichloropropene (top) and (E)-1,3-dichloropropene (bottom) in the soil of field DA. TR=transformed; REM=remaining in soil profile of 0.5 m; VOLA=volatilized. The line for downward diffusion to below 0.5 m (DDIF) coincides with the time axis.

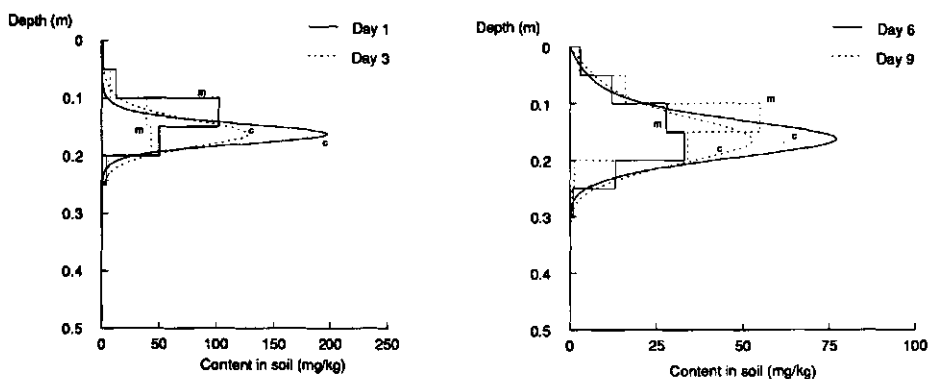


Fig. 11 Measured and simulated spread of (Z)-1,3-dichloropropene in the soil of field DB at four intervals after application. m=measured. c=calculated.

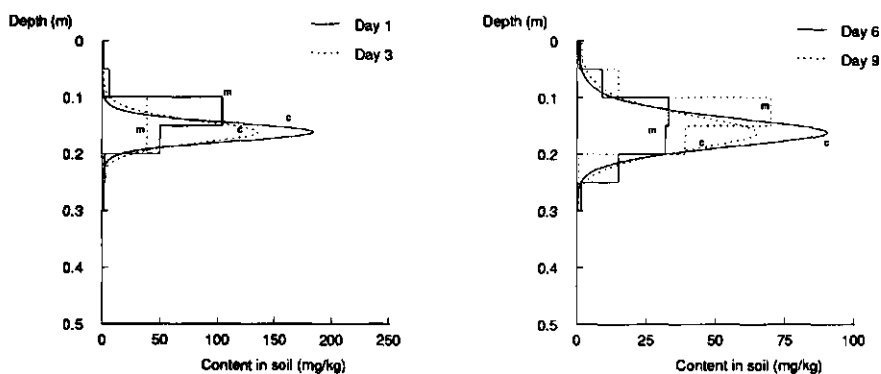


Fig. 12 Measured and simulated spread of (E)-1,3-dichloropropene in the soil of field DB at four intervals after application. m=measured. c=calculated.

Table XI: Measured and computed contents of 1,3-dichloropropene in the 0.0 - 0.05 m layer of the soil of field DB.

| Days after Injection | Content (mg kg ⁻¹) | |
|----------------------|--------------------------------|----------|
| | measured | computed |
| 1 | 1.9 | 0.0 |
| 3 | 0.4 | 0.5 |
| 6 | 3.9 | 2.6 |
| 9 | 4.5 | 4.4 |

content for the 0.10 - 0.20 m layer was considered, a somewhat higher content was computed than was measured. On the third and sixth days after the day of injection, the contents computed for the 0.10 - 0.20 m layer were higher than those measured, but on the ninth day the computed content was about the same as that measured.

The contents measured and computed for the 0.0 - 0.05 m layer are presented in Table XI. On the first day after the day of injection, the content calculated for this layer was lower than that measured. On the following days, the contents computed for this layer corresponded roughly to those measured. Throughout the whole sampling period, the contents computed for the 0.30 - 0.35 m layer corresponded with those measured: they were less than 0.3 mg kg⁻¹.

From the day of application onwards, the content of [(Z) plus (E)]-1,3-dichloropropene measured in the 0.10 - 0.15 m layer decreased steadily. However, on the ninth day after the day of application, the content measured in this layer was higher than that on the sixth day. This may have resulted from an uneven distribution of fumigant within a fumigated strip, caused by the spray pattern of the nozzles of the injection apparatus.

Data on the fate of 1,3-dichloropropene after injection into the soil of field DB are summarized in Figure 13. It was calculated that on the ninth day after the day of application, the amounts of (Z)- and (E)-1,3-dichloropropene remaining would be 60% and 68% of the dosage; this was not very different from the values measured on that day, i.e. 55% and 76%, respectively. It was calculated that 27% of the (Z)-isomer and 38% of the (E)-isomer remained after a period of 21 days.

The ratio of the (Z)- to the (E)-isomer in the product used for fumigating the soils is approximately 1.2. On the first day after the day of application, the ratios calculated and measured for the 0.15 - 0.20 m layer were still close to this value for both soils: 1.0. Above this layer in the soil profile, the ratio changed in favour of the (Z)-isomer. This can be attributed to the higher volatility of the (Z)-isomer. Up

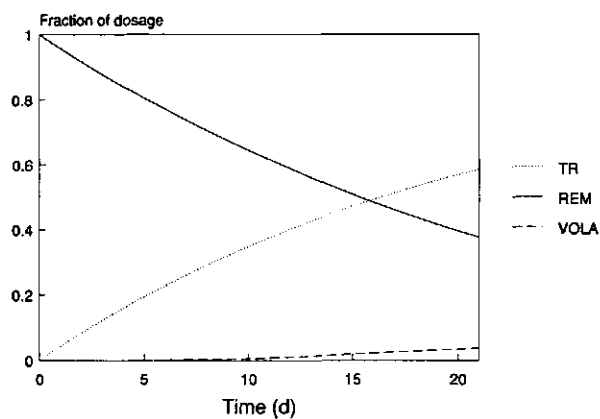
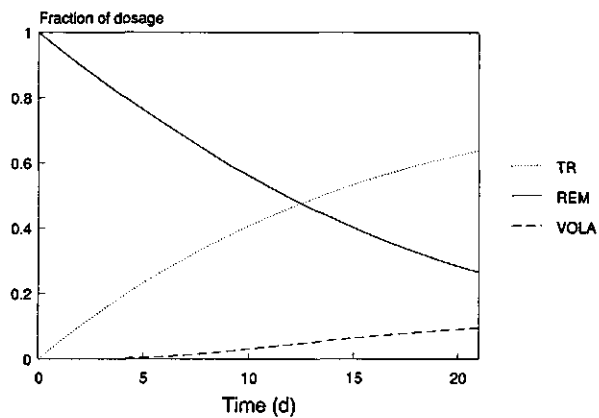


Fig. 13 Simulated fate of (Z)-1,3-dichloropropene (top) and (E)-1,3-dichloropropene (bottom) in the soil of field DB. TR=transformed; REM=remaining in soil profile of 0.5 m; VOLA=volatilized. The line for downward diffusion to below 0.5 m (DDIF) coincides with the time axis.

to nine days after application, the ratio calculated for the 0.0 - 0.05 m layer of field DA was greater than that for the product. For field DB the length of this period was 16 days. Thereafter, it decreased to below that value. During the period the soil samples were taken, the ratios measured for the 0.0 - 0.05 m and 0.05 - 0.10 m layers were generally higher than the ratio for the product. This corresponds with the computed ratios. At the end of the sampling period, the computed as well as the measured ratio for the 0.15 - 0.20 m layer had decreased to below unity, as expected.

8.3.2 Content patterns of methyl isothiocyanate

The contents of methyl isothiocyanate measured in the soil of field MA as well as those computed are presented in Figure 14. The injection depth was measured to be approximately 0.18 m. On the second day after the day of injection, the content measured in the 0.15 - 0.20 m layer was higher than that in the 0.20 - 0.25 m layer, but three days later the contents in these layers were about the same. On those days, much lower contents were measured for the 0.0 - 0.05 m layer: they remained below the determination limit, i.e. 1.1 and 1.5 mg kg⁻¹, respectively. The fumigant was measured to spread into deeper soil layers. On the fifth day after the day of application, the content measured in the 0.25 - 0.30 m layer was higher than that measured on the second day.

On the second day after the day of application, the highest contents of methyl isothiocyanate calculated were for both the 0.15 - 0.20 m and 0.20 - 0.25 m layers. For the 0.15 - 0.20 m layer, the content measured in the field was about the same as that computed, but for the 0.20 - 0.25 m layer the content measured was lower. On the fifth day, a large fraction of the fumigant was calculated to be in the 0.20 - 0.25 m, 0.25 - 0.30 m, and 0.30 - 0.35 m layers. The content measured in the 0.20 - 0.25 m layer was about the same as that computed, but in the other layers the contents measured were lower than those computed. On the second and fifth days, the contents calculated for the 0.0 - 0.05 m layer were higher than those measured: they were 3.0 and 4.9 mg kg⁻¹, respectively.

The computed downward diffusion was greater than that measured. This may have been caused by an underestimation of the adsorption of fumigant onto the solid phase of the 0.30 - 0.35 m layer. Presumably, the organic matter content in that layer was higher than that in the plough layer (see Section 2), which was used to calculate the ratio for the partitioning of fumigant between the solid and liquid phases in the standard model.

Data on the fate of methyl isothiocyanate in the soil of field MA are summarized in Figure 15. On the fifth day after the day of application, the amount of fumigant remaining in the whole soil profile was calculated to be 63% of the dosage, which is higher than the 37% of the dosage measured in the 0.0 - 0.35 m layer in the field on that day. It was calculated that 14% of the dosage remained after a period of 21 days.

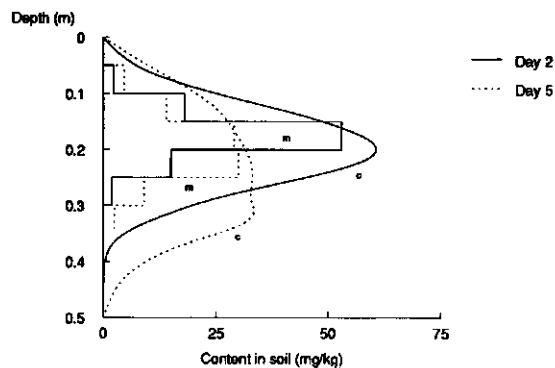


Fig. 14 Measured and simulated spread of methyl isothiocyanate in the soil of field MA at two intervals after application. m=measured. c=calculated.

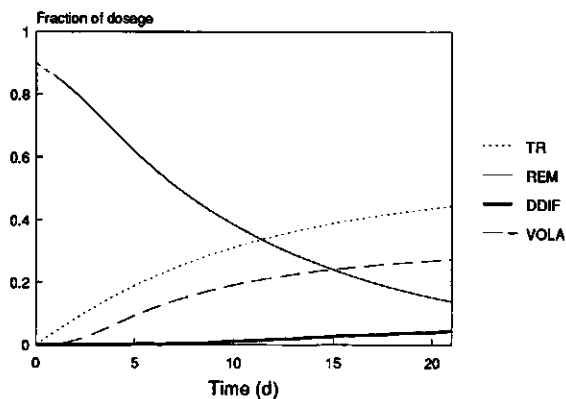


Fig. 15 Simulated fate of methyl isothiocyanate in the soil of field MA. TR=transformed; REM=remaining in soil profile of 0.5 m; DDIF=downward diffusion to below 0.5 m; VOLA=volatilized.

The measured and computed contents for field MB are presented in Figure 16. The injection depth measured for this field was approximately 0.18 m. On the second day after the day of application, the contents measured in the 0.10 - 0.15 and 0.20 - 0.25 m layers were substantially lower than that measured in the 0.15 - 0.20 m layer, but five days later the differences between these layers were smaller. On the second and seventh days, the contents measured for the 0.0 - 0.05 and 0.30 - 0.35 m layers remained below the determination limit, i.e. 0.8 mg kg^{-1} .

On the second and seventh days after the day of application, the contents calculated for the 0.15 - 0.20 m layer were substantially lower than those measured in the field. However, on the second and seventh days, the contents calculated for the 0.0 - 0.05 m layer were higher than those measured: the contents calculated were 1.2 and 3.8 mg kg^{-1} , respectively, whereas those measured remained below the determination limit. On the second day after the day of application, the content calculated for the 0.30 - 0.35 m layer corresponded with that measured, but five days later was somewhat higher.

Data on the fate of methyl isothiocyanate in the soil of field MB are summarized in Figure 17. For the seventh day after the day of application, the calculated and measured amounts of the dosage remaining in the soil profile down to 0.35 m were 59% and 63%, respectively. It was calculated that 20% of the dosage remained after a period of 21 days.

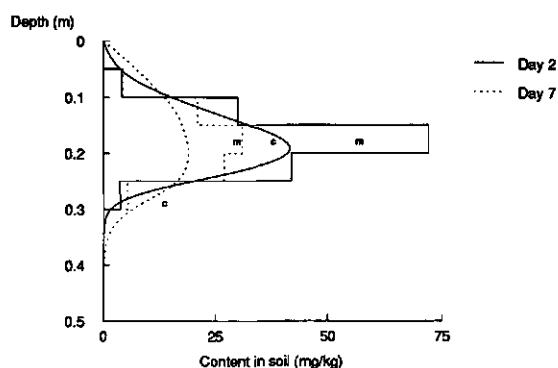


Fig. 16 Measured and simulated spread of methyl isothiocyanate in the soil of field MB at two intervals after application. m=measured. c=calculated.

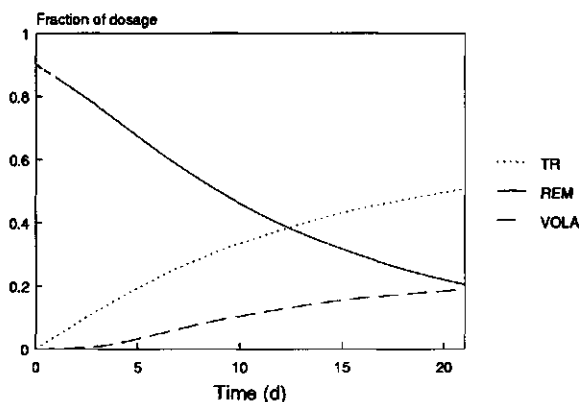


Fig. 17 Simulated fate of methyl isothiocyanate in the soil of field MB. TR=transformed; REM=remaining in soil profile of 0.5 m; VOLA=volatilized. The line for downward diffusion to below 0.5 m (DDIF) coincides with the time axis.

8.4 Discussion

The content patterns in soil computed for 1,3-dichloropropene indicated for both fields that the contents measured around the injection depth were lower than those computed. In the first few days, the measured upward movement of fumigant in the soil of field DA tended to be greater than that computed; in the soil of field DB the difference was less clear. From the fifth day after injection onwards, the computed downward diffusion in the soil of field DA was somewhat greater than that measured. No such difference was found for the soil of field DB. In general, the penetration of fumigant to depths of around 0.3 m was small, both in the computations and in the measurements.

Around the depth of injection, the ratio of the (Z)-isomer to the (E)-isomer decreased with time. Near the soil surface the ratio was greater than that in the applied mixture. Such changes in the ratios were expected because of the higher volatility of the (Z)-isomer.

The change in the content profile of 1,3-dichloropropene in soil with time as measured in the field was not always as expected. This may have been caused by local differences in the depth of injection or by an uneven distribution of the fumigant. This complicated the comparison of the computed content profiles with

those measured, as in the model a constant depth of injection and an even distribution were assumed.

The greater upward movement of 1,3-dichloropropene in the soil of field DA, compared with that simulated with the model, may have been caused by heterogeneities in soil structure. Pulling the injector blades through the soil or remnants of the previous crop in the plough layer may have resulted in such heterogeneities. The effect of heterogeneities in the soil structure such as clods on the movement of 1,3-dichloropropene through the soil can be substantial (Leistra, 1972). In a study on the fate of 1,3-dichloropropene in soil after its injection, Smelt et al. (1989b) found the coefficient of variation in replicated measurements of fumigant content in soil to range from 14 to 98%. Presumably, clods and looser parts in the soil contributed to the variance. The description of the soil structure as introduced in the standard model, assuming each soil layer of 0.05 m to be homogeneous, may have been too simple.

For the soil of field MA, the computed contents of methyl isothiocyanate around the injection depth tended to be higher than those measured, but for the soil of field MB the computed contents tended to underestimate the actual contents. For both fields, the computations indicated a greater diffusion of methyl isothiocyanate to the soil surface than was measured. For the soil of field MB, there was little penetration to depths below 0.30 m, both in the measurements and in the computations. The computed downward diffusion in the soil of field MA was greater than that measured.

Overestimation of the upward diffusion of methyl isothiocyanate by the model would result in an overestimation of the emission of this fumigant to the atmosphere. The most relevant simplification in the model could be that the rate coefficient for transformation of methyl isothiocyanate was assumed to be the same at all contents (first-order concept). Using this reasoning, the transformation potency in soil is assumed to be constant. However, in recent years complications in transformation kinetics have appeared, for example the dependency of the rate coefficient on the initial content of the fumigant. The rate coefficient for transformation of methyl isothiocyanate in a sandy soil was measured to be comparatively high at low initial contents of this fumigant in soil (Smelt and Groen, 1988). This would imply that the transformation of fumigant at some distance from the injection depth is faster than would be expected from the results of laboratory studies. Moreover, the initial content of methyl isothiocyanate in the incubations (Section 3.2) for soil sampled from field MA was relatively high compared with that in the field, assuming the dosage to be uniformly distributed throughout a 0.2 m arable layer. Another possible complication is the acceleration of the microbial transformation, induced by previous applications (see Section 3.1). Such an acceleration may start sooner at the comparatively low contents in the soil surface layer. The possible overestimation of the emission of methyl isothiocyanate to the air and the new data on the kinetics of transformation in soil prompted additional computations with a new submodel for fumigant transformation which is described in the next section.

9 IMPROVED SIMULATION FOR METHYL ISOTHIOCYANATE IN SOIL

9.1 Introduction

The computations on the spreading of methyl isothiocyanate in soil indicated comparatively high contents near the soil surface (in the top 0.05 m layer), compared with the limited number of measurements (Section 8). Consequently, an overestimation of the source strength of the emission of this fumigant into the air can be expected. One of the possible causes for this overestimation is a dependency of the rate coefficient of transformation of fumigant in soil on the fumigant content. Recently, Smelt and Groen (1989, personal communication) measured higher rates of transformation of methyl isothiocyanate in soil when initial fumigant contents were lower. Their data were used to make a new submodel for the transformation of this fumigant in soil, which was subsequently inserted in the standard model (Sections 4 to 6).

9.2 Procedures

Smelt and Groen (1989, personal communication) measured the rate of transformation of methyl isothiocyanate at various initial contents in soil from the top 0.2 m layer of a field near Buinen and in that of a field near Taarlo. These fields are located in the same area in the northeast of the Netherlands as those studied in this report. The content-dependency of the transformation rate coefficient (15 °C) could be linearized for starting contents in the range of 5 to 125 mg kg⁻¹ by plotting the log(rate coefficient) against the log(starting content). This linearity was used to obtain values for the transformation rate coefficient at starting contents above 125 mg kg⁻¹ by extrapolation. Below 5 mg kg⁻¹, the increase in the rate coefficient with decreasing starting content was less than that in the range of 125 to 5 mg kg⁻¹. For a decrease in starting content from 5 to 1 mg kg⁻¹, the rate coefficient was multiplied by 2.8 and for a decrease from 1 to 0.2 mg kg⁻¹ was multiplied by 1.5. The same rate coefficient was used for fumigant contents at and below 0.2 mg kg⁻¹. It should be noted that the number of measurements on the rate coefficient at low initial contents of fumigant in soil (around 0.2 mg kg⁻¹) was very limited.

The transformation rate coefficients measured for methyl isothiocyanate in soil of fields MA and MB at initial contents of 100 or 30 mg kg⁻¹, respectively, were chosen as the reference points to calculate the rate coefficients at various fumigant contents in soil. The dependency of content was assumed to correspond with the average of the relationships for the topsoils of the Buinen and Taarlo fields. The rate coefficients estimated for the two fields in the present study are given in Table XII. These data were introduced into the modified model for fumigant behaviour in soil, using a FUNCTION statement. A value for the rate coefficient was obtained for every fumigant content in soil by linear interpolation. The other parts of the computer-simulation model were the same as those described in Sections 4 to 6.

Table XII: Estimated rate coefficients for the transformation of methyl isothiocyanate at various starting contents in the soils of fields MA and MB. The values apply to the temperature of the plough layer at the time of fumigation.

| Starting content (mg kg ⁻¹) | Rate coefficient (d ⁻¹) | |
|--|-------------------------------------|-----------------------|
| | Field MA | Field MB [*] |
| 1000 | 0.005 | 0.002 |
| 500 | 0.010 | 0.003 |
| 200 | 0.022 | 0.008 |
| 100 | 0.042** | 0.015 |
| 50 | 0.080 | 0.028 |
| 20 | 0.185 | 0.065 |
| 10 | 0.350 | 0.124 |
| 5.0 | 0.664 | 0.235 |
| 1.0 | 1.9 | 0.657 |
| 0.2 | 2.8 | 0.98 |

^{*}) Rate coefficient measured for soil of field MB at an initial content of 30 mg kg⁻¹: 0.045 d⁻¹.

^{**}) Rate coefficient measured (Section 3).

Presumably, microbial activity resulting in the transformation of methyl isothiocyanate is inhibited at higher fumigant contents in soil. However, the measurements of Smelt and Groen (1989, personal communication) suggest no straightforward relationship between fumigant content and transformation rate. Rather, a certain initial content seems decisive for the rate coefficient of transformation in the first one to two weeks. Therefore, the rate coefficient in a computation compartment at each time step was calculated from the highest content recorded in that compartment up to the time of simulation.

9.3 Results and discussion

The contents in soil computed for field MA using the modified model are presented in Figure 18. On the second day after the day of application, the contents calculated for the 0.15 - 0.20 m and 0.20 - 0.25 m layers were similar to those calculated earlier (Section 8.3.2). On the fifth day, the contents computed for the 0.20 - 0.25 m, 0.25 - 0.30 m, and 0.30 - 0.35 m layers were lower than those in the earlier computations, but the contents in the two latter layers were still higher than those measured.

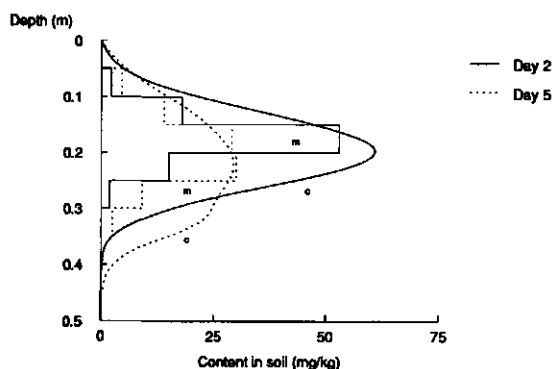


Fig. 18 *Measured and simulated spread of methyl isothiocyanate in the soil of field MA at two intervals after application. Rate coefficient of transformation dependent on the highest preceding content. m=measured. c=calculated.*

On the second and fifth days, the contents calculated for the 0.0 - 0.05 m layer were lower than those calculated before. The newly computed contents were still somewhat higher than those measured, which were below the determination limit (ranging from 1.1 to 1.5 mg kg⁻¹). The computed diffusion to depths below 0.4 m was lower than that computed with the standard model, so the newly computed contents corresponded somewhat better with the measurements.

Data on the fate of methyl isothiocyanate in the soil of field MA are summarized in Figure 19. On the fifth day, the amount of fumigant remaining was calculated to be 49%, which is higher than that measured in the field (37%), but lower than that calculated previously (63%). It was calculated that in the whole soil profile 3.2% of the dosage remained after a period of 21 days.

The content patterns in soil computed for field MB using the modified model are presented in Figure 20. On the second and seventh days after the day of application, the calculated contents around the day of injection were similar to those computed previously, so they remained lower than those measured in the field. On the second and seventh days, the contents calculated for the 0.0 - 0.05 m layer were lower than those calculated previously. The new contents corresponded more favourably with the measurements, albeit that on the seventh day after the day of injection, the content computed for this layer was still somewhat higher than that measured (below the determination limit of 0.8 mg kg⁻¹).

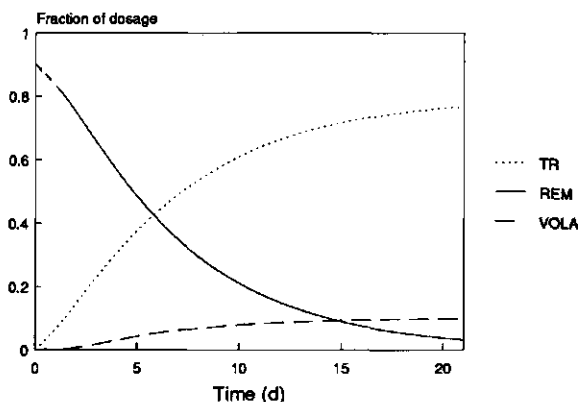


Fig. 19 Simulated fate of methyl isothiocyanate in the soil of field MA. Rate coefficient of transformation dependent on the highest preceding content. TR=transformed; REM=remaining in soil profile of 0.5 m; VOLA=volatilized. The line for downward diffusion to below 0.5 m (DDIF) coincides with the time axis.

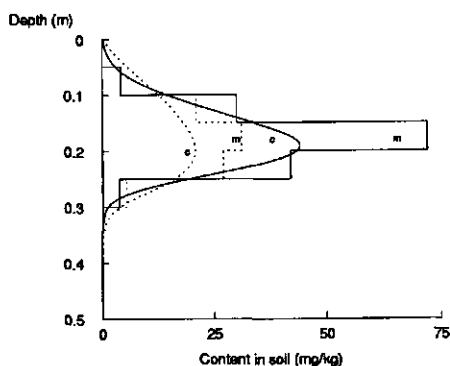


Fig. 20 Measured and simulated spread of methyl isothiocyanate in the soil of field MB at two intervals after application. Rate coefficient of transformation dependent on the highest preceding content. m=measured. c=calculated.

Data on the fate of methyl isothiocyanate in the soil of field MB are summarized in Figure 21. On the seventh day, the calculated and measured amounts remaining in the soil profile were 55% and 63% of the dosage, respectively. It was calculated that in the whole soil profile 13% of the dosage remained after a period of 21 days.

The computed rates of emission of methyl isothiocyanate from the soil of the two fields to the atmosphere are presented in Figure 22. The maximum values computed for this rate were $116 \text{ mg m}^{-2} \text{ d}^{-1}$ for field MA (on day 3) and $83 \text{ mg m}^{-2} \text{ d}^{-1}$ for field MB (on day 6). Three weeks after injection of metham-sodium, the computed rate of emission from the soil of field MA had decreased to 5% of its maximum value and that for the soil of field MB had decreased to 23% of its maximum value.

The cumulative loss by volatilization is expressed as the percentage of the equivalent dosage of methyl isothiocyanate corresponding to the actual dosage of its precursor metham-sodium. The values computed for this cumulative loss, at weekly intervals, are presented in Table XIII.

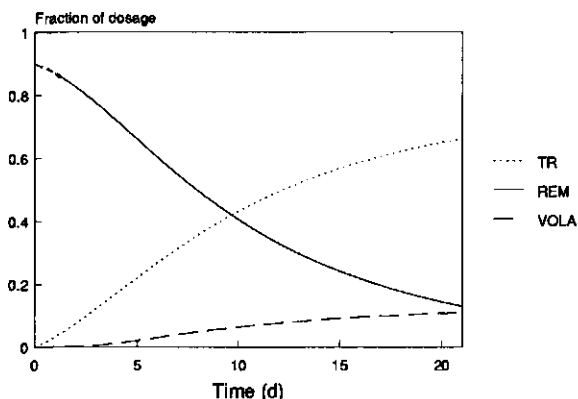


Fig. 21 Simulated fate of methyl isothiocyanate in the soil of field MB. Rate coefficient of transformation dependent on the highest preceding content. TR=transformed; REM=remaining in soil profile of 0.5 m; VOLA=volatilized. The line for downward diffusion to below 0.5 m (DDIF) coincides with the time axis.

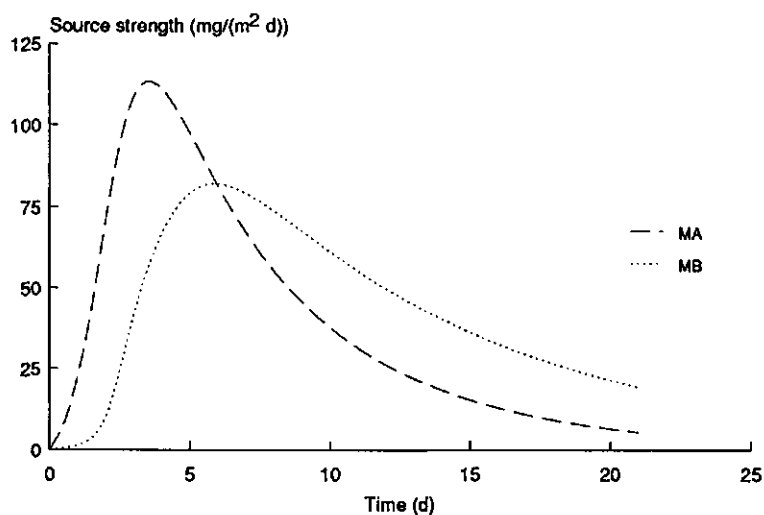


Fig. 22 Rate of emission of methyl isothiocyanate from soil to air computed for fields MA and MB. Rate coefficient of transformation dependent on the highest preceding content.

The values computed with the modified model are distinctly lower than those computed with the standard model (Section 7.2, Table IX). The greater emission reduction computed for field MA (from 27 to 10%) can be explained by the fact that the rate coefficient of transformation of methyl isothiocyanate in soil from field MA was measured at an initial content of 100 mg kg^{-1} dry soil, whereas in soil from field MB it was measured at an initial content of 30 mg kg^{-1} . These measured values have been used in the model with constant rate coefficient. If the same relative content-dependency of the rate coefficient is introduced in the model, the range of the rate coefficient of transformation at fumigant contents in soil below that of the incubation study is thus greater for field MA than for field MB.

Table XIII: Percentage of the equivalent dosage of methyl isothiocyanate computed to be lost by volatilization from the soil of the fields studied using the model with modified transformation kinetics.

| Field | Cumulative volatilization (%) after | | |
|-------|-------------------------------------|---------|---------|
| | 1 week | 2 weeks | 3 weeks |
| MA | 6.1 | 9.1 | 9.9 |
| MB | 3.9 | 8.6 | 11 |

The differences between the contents of methyl isothiocyanate in soil computed with the modified model and those measured on a limited scale in the field are smaller than those for the earlier computations. Therefore, the course of the rate of emission of methyl isothiocyanate into the air with time, as calculated with the modified model, can be expected to correspond more favourably with the actual course than that calculated with the standard model.

10 COMPUTED EFFECT OF RAINFALL AND EVAPORATION ON EMISSION INTO THE AIR

10.1 Introduction

In the standard simulation model (Sections 4 to 6), rainfall and evaporation were not taken into account. Because the rate of emission into the air depends on the rate of diffusion of fumigant in the soil surface layer, changes in soil moisture content due to rainfall and evaporation may affect this rate substantially. To assess the impact of changes in soil moisture content on the emission, computations are needed using a model which describes the flow of water in the soil as well as the transport of chemicals. For the present purpose, the model developed by Boesten (1986) was taken as a starting point. This model was extended and modified to include the transport of fumigant by diffusion through the gas-filled pore system. As the purpose of this study was to obtain some insight into the impact of simplifications in the standard model on the emission of fumigant into the air, computations were only done for (Z)-1,3-dichloropropene in the soil of one field.

10.2 Model description and input parameters

The model developed by Boesten (1986) describes the leaching and accumulation of non-volatile pesticides in soil. In this model, it is assumed that rainwater infiltrating the soil fills the soil layers with water from top to bottom up to field capacity. When the rainfall ceases, it is assumed that there is no redistribution of soil moisture. During evaporation of water at the soil surface, it is assumed that the withdrawal of water from a certain depth is proportional to the evaporation flux density at the soil surface, the volume fraction of liquid and a withdrawal factor which decreases with increasing soil depth. More details on the description of the flow of water in soil is given by Boesten (1986, Chapter 5). The transport of pesticides through the soil was considered to occur by convection with liquid flow, by convective dispersion in the liquid phase and by diffusion through that phase. The isotherm for the adsorption of pesticide from the liquid phase onto the solid phase was described using a Freundlich equation. Further, the transformation of pesticides in soil was assumed to follow first-order kinetics.

To describe the behaviour of volatile pesticides in soil, i.e. the soil fumigant (Z)-1,3-dichloropropene, the following modifications were introduced into the model developed by Boesten (1986). The coefficient of the Freundlich equation was taken to be 1.0, which results in the equation describing linear adsorption as used in the standard model (see Section 4). It was assumed that equilibrium existed in the partitioning of fumigant between the soil phases at all times. The model section containing the pesticide transport equations was modified to include the transport of fumigant by diffusion through the gas phase. Another modification was that the fumigant was introduced into the soil compartment corresponding to the injection depth instead of being applied at the soil surface. For the present study, the

fumigation of field DA with 1,3-dichloropropene was selected to assess the effect of rainfall and evaporation on fumigant behaviour in soil. The computations are done for the (Z)-isomer, which is the most volatile of the two isomers of 1,3-dichloropropene. The simulation period was the first three weeks following injection.

Values for the first-order rate coefficient of transformation of (Z)-1,3-dichloropropene, its coefficient of diffusion in air and ratios for the partitioning of this fumigant between the soil phases were the same as those introduced in the standard model. Values of the tortuosity factor for the diffusion through the gas-filled pore system as a function of the volume fraction of the gas phase were also the same as those used in the standard model. Using a method described by Reid and Sherwood (1966, p. 550), the coefficient of diffusion of 1,3-dichloropropene in water was calculated to be $0.52 \cdot 10^{-4} \text{ m}^2 \text{ d}^{-1}$. Values of the tortuosity coefficient for diffusion through the liquid phase of the soil system as a function of the volume fraction of liquid phase were those used by Boesten (1986). The value for the dispersion length was taken as 0.008 m, which is an intermediate value in the range evaluated by Boesten (1986).

Like the standard model presented in Section 6, the model developed by Boesten (1986) is written in the CSMP computer language. Therefore, the way in which values for the input parameters were introduced was similar in both models. As in the standard model, a soil profile with a depth of 0.5 m was considered. The thicknesses of the compartments in the top 0.15 m layer were the same as those introduced by Boesten (1986): 0.005 and 0.01 m for the 0.0 - 0.05 and 0.05 - 0.15 m layers, respectively. The thickness of each compartment below this depth was 0.025 m, which is equal to the thickness of a compartment in the standard model. In the modified model, the fumigant (Z)-1,3-dichloropropene was introduced in the 22nd compartment from the top, which coincides with the 8th compartment from the top in the standard model (see Section 5).

Data on the daily amounts of rainfall used in the computations were taken from measurements at a site near field DA and are presented in Figure 23. These data were introduced into the model in TABLE form. Data on the daily amounts of water evaporation from soil need to be introduced into the model and can be calculated from the daily amounts of water evaporation from an open water surface, E_0 , using a model described by Boesten and Stroosnijder (1986). As no data on E_0 for the simulated period were available, they were estimated from daily values of the Makkink crop reference evaporation. During the summer months, there is a good correlation between this evaporation and E_0 (De Bruin, 1987). Although for October and November this correlation is rather poor, it could be used to obtain an estimate of E_0 (De Bruin, 1987). Daily values of the Makkink evaporation were obtained from the Royal Netherlands Meteorological Institute (KNMI, 1987). The input data on the daily amounts of evaporation from soil are given in Figure 24 and were introduced into the model in TABLE form.

Estimates were made of the volume fractions of water in each 0.05 m layer of the topsoil of field DA at field capacity. Shortly after injection on October 28, the volume fractions of liquid in the 0.15 - 0.35 m layer of field DA were measured to

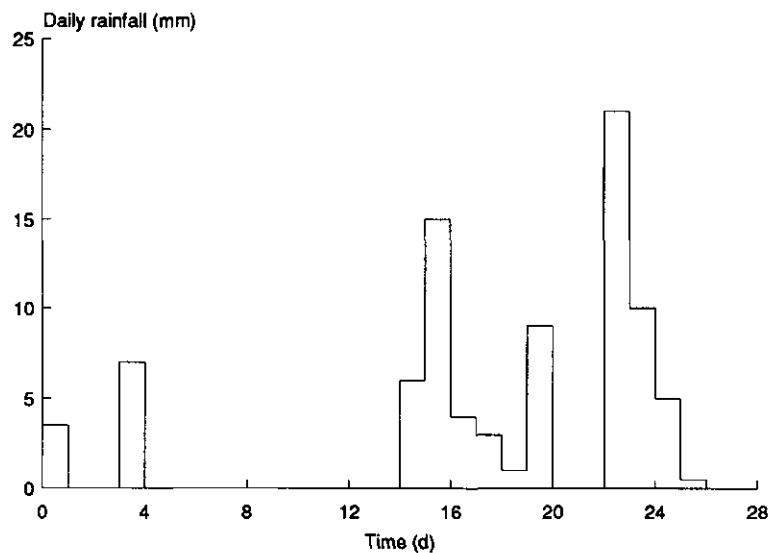


Fig. 23 Daily rainfall measured near field DA. Zero time= time of injection.

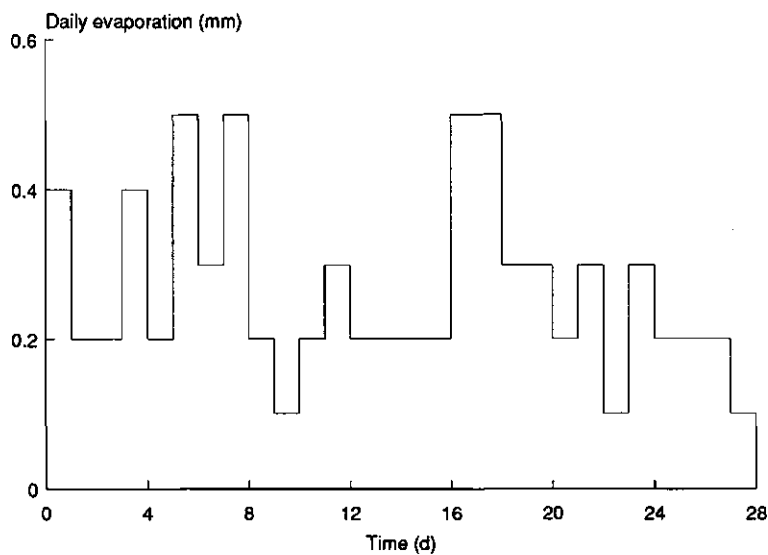


Fig. 24 Estimated daily evaporation from the soil of field DA. Zero time= time of injection.

be comparatively high compared with those for the 0.0 - 0.15 m layer (See Section 2, Table II). As in a period preceding the day of injection, i.e. from October 6 to October 16, about 65 mm rain was measured at a site near field DA, it was assumed that the topsoil of field DA had been at field capacity on October 16. A cumulative evaporation of about 6 mm was calculated for the dry period from October 16 to the day of injection using the method described by Boesten and Stroosnijder (1986). Equal portions of this amount were assigned to each 0.05 m layer in the top 0.15 m layer. The lower limit of the volume fraction of liquid phase in each compartment was taken to be 0.01, which is the same as the value used by Boesten (1986). Values for the bulk density and the initial volume fractions of the liquid and gas phases were introduced into the model in the same way as in the standard model (see Section 6).

At each time step, first the flow rate of liquid at the compartment boundaries, as caused by downward flow due to rainfall or upward flow due to evaporation, was calculated. The rate of change in the volume fraction of the gas phase in each compartment was taken to be equal to that of the liquid phase, but having an opposite sign. Subsequently, the partitioning of (Z)-1,3-dichloropropene over the soil phases was calculated. This enabled the calculation of the concentration gradients which were then used to calculate the fumigant fluxes between the compartments. The flux density of fumigant by convection with liquid across the compartment boundary was calculated by multiplying the volume flux density of liquid by the concentration of fumigant in the liquid phase at the boundary. The coefficient of dispersion in the liquid phase was calculated by multiplying the dispersion length by the volume flux density of liquid. The dispersion flux density was calculated by multiplying the coefficient of dispersion by the concentration gradient in the liquid phase. In each compartment, the coefficients for diffusion of fumigant through the liquid and gas phases were calculated from the volume fractions and the tortuosity factors of the corresponding phases. The coefficients of diffusion at the compartment boundaries were obtained by interpolation. The diffusion flux densities of fumigant through the liquid and gas phases were calculated by multiplying the coefficient of diffusion for each phase with the corresponding concentration gradient. Further statements were added to calculate the mass balance of pesticide (see Section 6). The rate of emission of pesticide into the air was calculated as described in Section 6.

A series of computations for a hypothetical pesticide was done to validate the extended model numerically. A soil system of 0.5 m depth was considered. The distribution between the soil phases was taken to be constant throughout the soil profile; the volume fractions of the liquid and gas phases being 0.42 and 0.27, respectively. The volume fraction of the liquid phase at field capacity was also taken to be 0.42. Further, a hypothetical daily amount of rainfall of 5 mm was taken and daily actual evaporation assumed to be zero. The initial content of the pesticide in the soil profile at $t = 0$ was zero. During the first day, the water infiltrating the soil contained pesticide at a concentration of 1.8 kg m^{-3} . Thereafter, the concentration in the infiltrating water was set at zero and its flux density at the soil surface was also set at zero. Transport of this hypothetical pesticide in soil was by convection, convective dispersion in the liquid phase, and diffusion in the gas and liquid phases. Its transformation was assumed to follow first-order kinetics. Values of the ratios

for the partitioning of the pesticide between the soil phases and that of the rate coefficient of transformation of pesticide were the same as those used to simulate the behaviour of (Z)-1,3-dichloropropene in the soil of field DA. The analytical solution to the resulting problem is given by Van Genuchten and Alves (1982). The content profile for the hypothetical pesticide in the soil was calculated twice, i.e. after 7 and 21 days. The content profiles obtained from the analytical solution were compared with those computed with the numerical model. The results obtained for 7 days are shown in Figure 25 and those for 21 days in Figure 26. There is good agreement between the contents in soil as computed with the computer-simulation model and those computed with the solution to the one-dimensional conservation equation given by Van Genuchten and Alves (1982). It should be noted that the contents of pesticide in the soil surface layer as shown in Figure 26 have not yet decreased to zero. Such a decrease can be expected later and this is also described by the Van Genuchten and Alves equation.

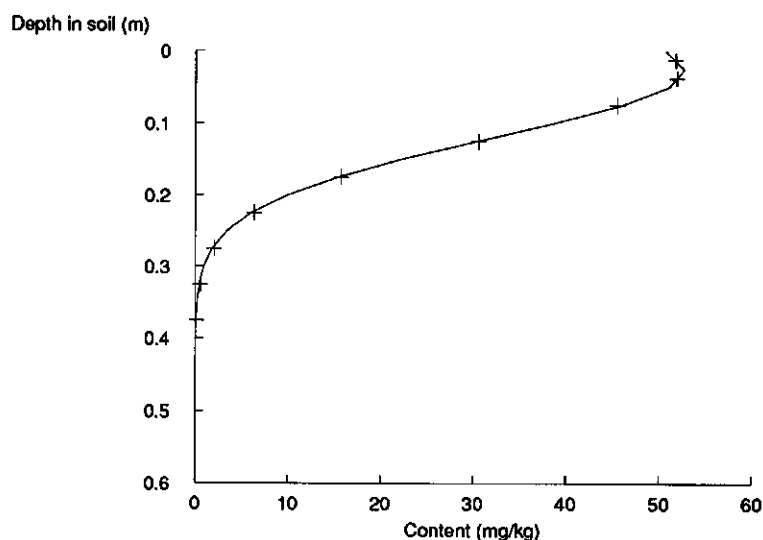


Fig. 25 *Computed content of a hypothetical pesticide in soil at $t=7.0$ days. Solid line= computed according to Van Genuchten and Alves (1982, eq. C6). + = computed with extended model of Section 10.*

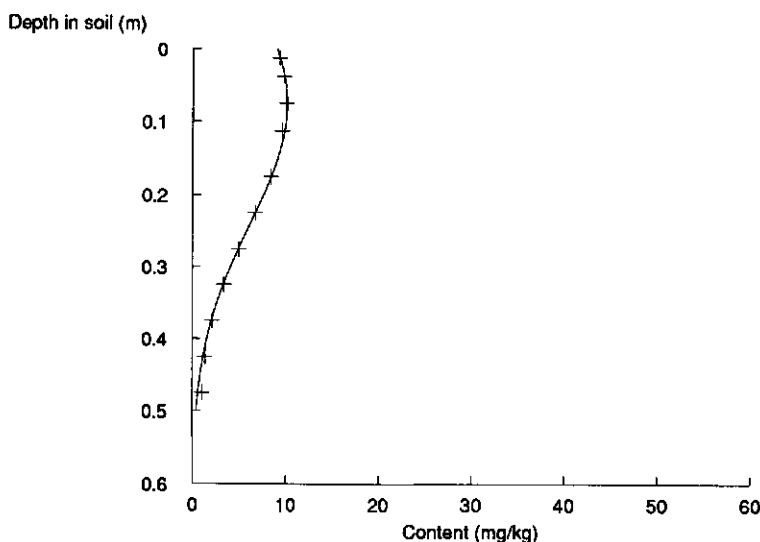


Fig. 26 Computed content of a hypothetical pesticide in soil at $t=21.0$ days. Solid line= computed according to Van Genuchten and Alves (1982, eq. C6). + = computed with extended model of Section 10.

10.3 Results and discussion

The course of the rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air, as computed with the modified model, is presented in Figure 27. In this figure, the course of the rate of emission as computed with the standard model is given for comparison. Due to rainfall during the first and fourth days after injection (see Figure 23), a substantially lower maximum rate of emission is reached compared with that computed with the standard model (124 versus $178 \text{ mg m}^{-2} \text{ d}^{-1}$). The lower rates of emission can be explained by the decrease in the volume fraction of the gas phase in the soil surface layer and the downward convective transport of fumigant with the liquid phase caused by the infiltrating rain.

The effects of rainfall and evaporation on the computed cumulative emission into the air are illustrated in Figure 28. The cumulative emission during the first three weeks computed with the standard model was 22%, but when rainfall and evaporation were taken into account, it decreased to 16%.

The modified model was checked by setting values for daily amounts of rainfall and evaporation at zero. All other input data remained the same as for previous computations. The computed course in the rate of emission of (Z)-1,3-dichloropropene into the air with time coincided with that computed with the standard model, so under constant soil moisture conditions both models give identical results.

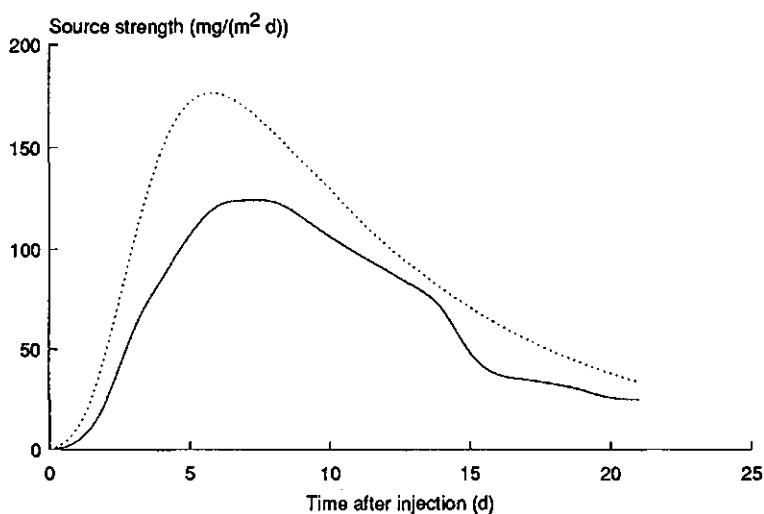


Fig. 27 *Computed effect of rainfall and evaporation on the rate of emission of (Z)-1,3-dichloropropene from the soil of field DA. Dotted line = computed with standard model.*

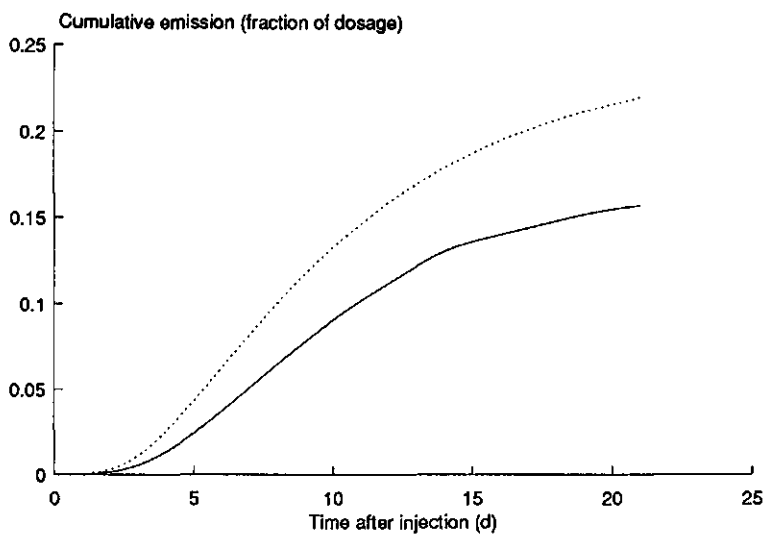


Fig. 28 *Computed effect of rainfall and evaporation on the cumulative emission of (Z)-1,3-dichloropropene from the soil of field DA after injection. Dotted line = computed with standard model.*

11 COMPUTED EFFECT OF TEMPERATURE CHANGES ON EMISSION INTO THE AIR

11.1 Introduction

In the standard model an isothermal soil system was considered. Values for temperature-dependent input parameters were calculated for the average soil temperature in the plough layer during the fumigation period. However, under field conditions there is a diurnal change in soil temperature and this is most pronounced near the soil surface. To assess the effect of variations in soil temperature on the emission of fumigant into the air, a description is needed of the course of the temperature at the soil surface and of the transfer of heat through the soil. Further, descriptions of the temperature-dependency of the processes most relevant for fumigant behaviour in soil need to be included. As changes in soil moisture content affect the thermal properties of the soil, a description of the dependence of these properties on moisture content is also required. Therefore, new submodels were made and inserted into the model as described in Section 10. The resulting model was used to assess the effect of diurnal changes in soil temperature on the rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air for the situation with rainwater infiltration described in Section 10. The effect of a diurnal temperature change on the course of the rate of emission from a soil with a constant moisture condition was also investigated.

11.2 Model description and input parameters

The transfer of heat through the soil occurs as a result of differences in soil temperature. Such transfer occurs mainly by conduction. The transfer of heat through the soil by conduction in the vertical direction can be described by:

$$J_{h,c} = - a \frac{\partial T}{\partial z} \quad (13)$$

in which:

$J_{h,c}$ = flux density of heat by conduction

(J m⁻²(soil) d⁻¹)

a = soil thermal conductivity

(J m⁻¹(soil) d⁻¹ K⁻¹)

Conduction of heat depends on the thermal properties of the soil: the thermal conductivity and the volumetric heat capacity. The contributions of the soil components to the thermal conductivity and the volumetric heat capacity of the soil vary widely (Van Wijk and De Vries, 1963).

Values for the volumetric heat capacity and the thermal conductivity of the plough layer of field DA at moisture contents ranging from air-dry to water-saturated were calculated using the method described by De Vries (1963). In the calculations,

average values were used for the bulk density and the organic matter content of the plough layer, i.e. 770 kg m^{-3} and 17%, respectively. Further, it was assumed that the mineral parts had the thermal properties of quartz. The thermal properties of the various soil materials at 10°C were taken from De Vries (1963). The calculated thermal conductivity and volumetric heat capacity as a function of the volume fraction of liquid are presented in Figures 29 and 30, respectively. These relationships were introduced into the initial part of the model with a FUNCTION statement.

Heat flux by liquid transport can be described by:

$$J_{h,l} = J_l^V \cdot Q_l \cdot T \quad (14)$$

in which:

$$J_{h,l} = \text{flux density of heat by transport of liquid} \quad (\text{J m}^{-2}(\text{soil}) \text{ d}^{-1})$$

$$J_l^V = \text{volume flux density of liquid phase by convection} \quad (\text{m}^3(\text{liquid}) \text{ m}^{-2}(\text{soil}) \text{ d}^{-1})$$

$$Q_l = \text{volumetric heat capacity of liquid} \quad (\text{J m}^{-3}(\text{liquid}) \text{ K}^{-1})$$

The conservation equation for heat in soil can be given as:

$$\frac{\partial Q_s \cdot T}{\partial t} = - \frac{\partial J_{h,c}}{\partial z} - \frac{\partial J_{h,l}}{\partial z} \quad (15)$$

in which:

$$Q_s = \text{volumetric heat capacity of the soil} \quad (\text{J m}^{-3}(\text{soil}) \text{ K}^{-1})$$

It was assumed that changes in temperature at the soil surface could be described with a sinusoidal function. The following equation can be used (Van Wijk and De Vries, 1963):

$$\phi(t) = \phi_s + \Delta\phi_0 \sin(f \cdot t + \beta) \quad (16)$$

in which:

$$\phi(t) = \text{temperature at the soil surface at time } t \quad (\text{K})$$

$$\phi_s = \text{average soil temperature} \quad (\text{K})$$

$$\Delta\phi_0 = \text{amplitude of temperature at the soil surface} \quad (\text{K})$$

$$f = \text{radial frequency of the temperature variation} \quad (\text{rad d}^{-1})$$

$$\beta = \text{phase constant} \quad (\text{rad})$$

The average temperature was taken to be 9°C , which is equal to the average temperature in the plough layer for which computations were done with the standard model. As diurnal changes in temperature were considered, f was taken to be $2\pi \text{ rad d}^{-1}$. The phase constant β indicates at which time during the day the maximum temperature is reached at the soil surface. In the present computations, it was assumed that the highest temperature at the soil surface was reached at noon, which results in a phase constant of $-\pi/2 \text{ rad}$. The daily amplitude was taken to be 5 K .

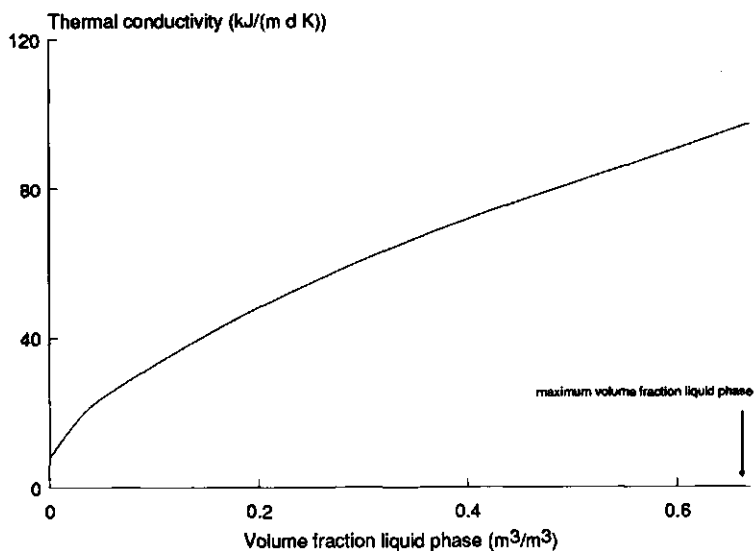


Fig. 29 Calculated thermal conductivity of the plough layer of field DA as a function of the volume fraction of liquid phase.

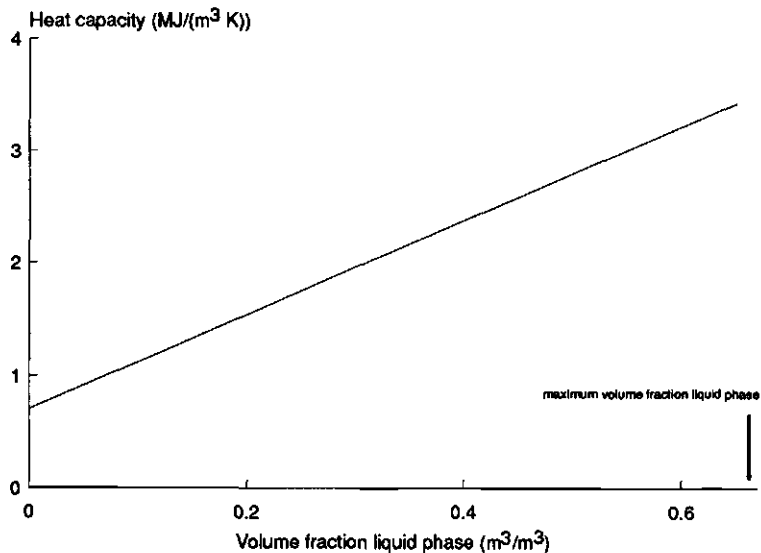


Fig. 30 Calculated volumetric heat capacity of the plough layer of field DA as a function of the volume fraction of liquid phase.

Equations (13) to (16) were transcribed in CSMP computer language and inserted as a submodel into the dynamic part of the model as described in Section 10. In this part, first the liquid fluxes were calculated. This enabled the possible transfer of heat through the soil by flow of liquid to be calculated. As there was no information on the temperature of the infiltrating rainwater, it was assumed that its temperature was the same as that at the soil surface. The thermal properties of each compartment were calculated using a function describing these properties as a function of the volume fraction of liquid phase. Then, the temperature in each compartment was calculated from its volumetric heat content, which enabled the heat flux densities at the compartment boundaries to be calculated.

When simulating a diurnal change in temperature, the starting temperature at $t = 0.00$ h in each compartment was obtained from the computed temperature profiles in the soil of field DA, when a temperature function (Eq. (16)) was imposed on the soil surface with an average temperature of 9°C and an amplitude of 5 K. In these computations, the distribution between the soil phases in the profile remained constant and the initial temperature in the whole soil profile was 9°C . The computations showed that the temperature profile at a particular time during the day was roughly the same after three days. Therefore, the temperature profile computed for midnight after three days was taken as the starting temperature profile at $t = 0.00$ h of the day of fumigant injection. The starting temperature profile for field DA, when taking the average temperature as 9°C and the amplitude as 5 K, is presented in Figure 31.

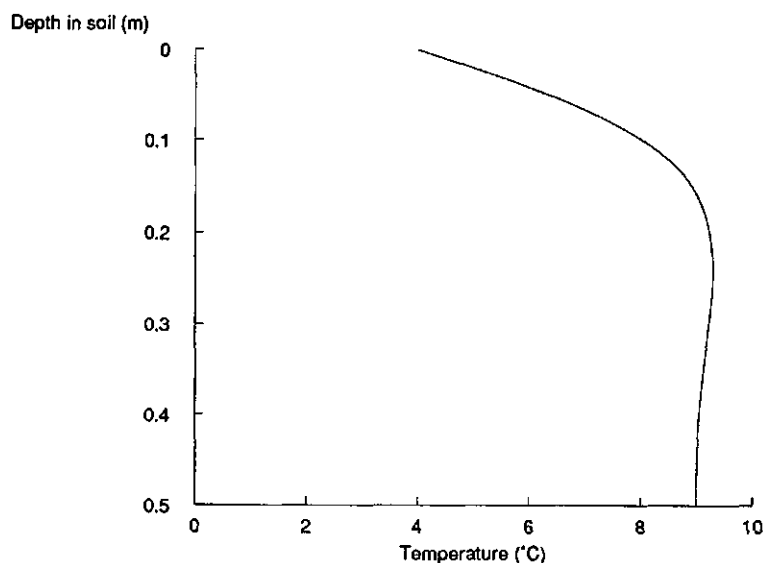


Fig. 31 Computed temperature profile in the soil of field DA at midnight.

The temperature-dependence of the linear adsorption coefficient, K_{ad} , and the ratio for the partitioning between the liquid and gas phases, K_{lg} , were introduced into the model in TABLE form. Values for these parameters at different temperatures were determined by Leistra (1972). To calculate the value of the first-order rate coefficient of transformation at a certain temperature, Equation (12) (Section 5.2) was transcribed into CSMP computer language and inserted into the dynamic part of the model. Because the effect of temperature on the coefficient of diffusion of 1,3-dichloropropene in air is comparatively small, an average value for this coefficient was taken, representative of the average temperature in the plough layer.

In the computations, the dosage was introduced into the system at the time of day at which half the field had been injected with 1,3-dichloropropene, i.e. at $t = 0.4$ d. At each time step, the values of the temperature-dependent parameters for each compartment were calculated from the prevailing temperature in that compartment. The computation procedure for the transformation and transport of fumigant in soil was the same as that described in Section 10.

A second series of computations was done to assess the effect of diurnal changes in soil temperature on the rate of emission of (Z)-1,3-dichloropropene into the air under constant soil moisture conditions. This was done by setting the input values for the daily rainfall and evaporation in the TABLES at zero.

11.3 Results and discussion

The course of the computed rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air is presented in Figure 32. In this figure, the course of the rate of emission as computed with the model described in Section 10 is given for comparison. The computations show substantial differences in the rate of emission of (Z)-1,3-dichloropropene into the air during the day, ranging up to a factor of approximately 1.5. Much higher rates of emission are computed at noon, when the computed soil surface temperature reaches its maximum, than at midnight, when the soil surface temperature is at its minimum.

The effect of diurnal changes in soil temperature on the computed cumulative emission into the air is illustrated in Figure 33. The cumulative emission during the first three weeks after injection was almost the same as that computed with the extended model of Section 10.

The effect of a diurnal change in soil temperature on the rate of emission under constant soil moisture conditions is illustrated in Figure 34. In this figure, the course of the rate of emission as computed with the standard model is also given. Similar differences are computed in the rate of emission during the day as under changing soil moisture conditions (see Figure 32).

The extended model was checked by setting the amplitude of the temperature at the soil surface at zero and the temperature in all soil compartments at 9°C . This resulted in a soil temperature profile being constant with depth and time. The course

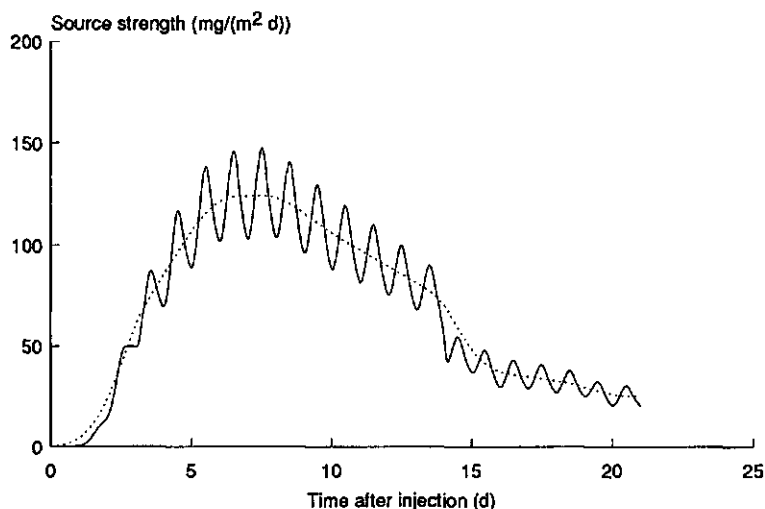


Fig. 32 *Computed effect of diurnal temperature variation on the rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air. Daily amplitude of temperature at the soil surface 5 K. Dotted line = computed with the extended model of Section 10.*

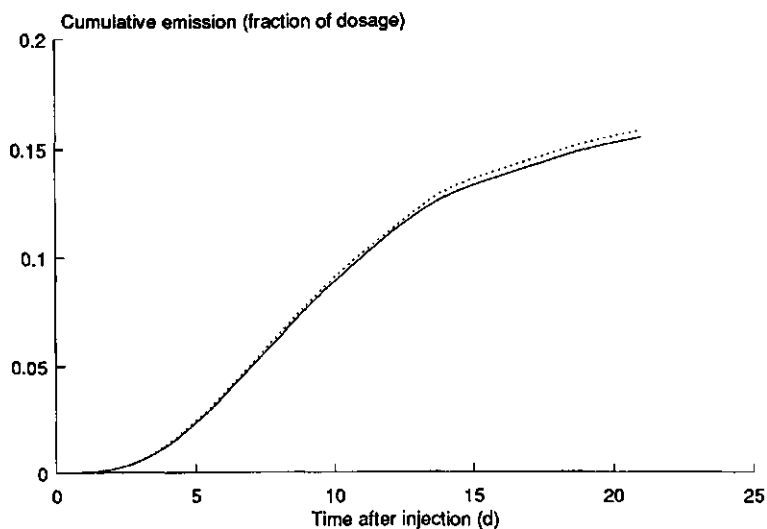


Fig. 33 *Computed effect of diurnal temperature variation on the cumulative emission of (Z)-1,3-dichloropropene from the soil of field DA into the air. Daily amplitude of temperature at the soil surface 5 K. Dotted line = computed with the extended model of Section 10.*

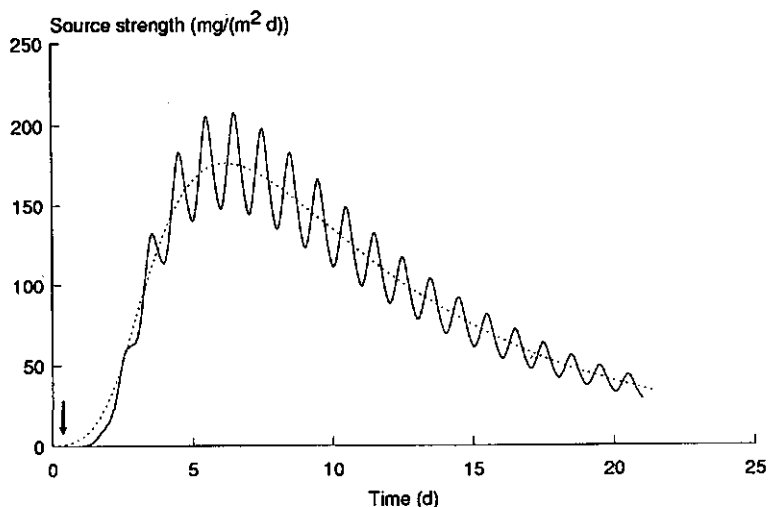


Fig. 34 *Computed effect of diurnal temperature variation on the rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air. Injection at $t=0.4$ d (indicated by arrow). Daily amplitude of temperature at the soil surface 5 K; soil moisture profile constant in time. Dotted line = computed with standard model.*

of the computed rate of emission of (Z)-1,3-dichloropropene from the soil of field DA into the air coincided with that computed with the model described in Section 10 (see Figure 27).

Cohen et al. (1988) simulated the volatilization of lindane after its incorporation into a dry silt loam soil (moisture content about 4% by mass) to a depth of 0.1 m. The transformation of lindane in soil was neglected. They considered an isothermal soil system at a temperature equal to the average of the top 0.2 m layer and a non-isothermal soil system with a daily temperature variation of 10 K at the surface. During a period of ten days following application, the percentages of the dosage of lindane computed to be lost by volatilization under isothermal and non-isothermal conditions were 2.0 and 2.2%, respectively. This comparatively small difference between the fractions of the dosage lost by volatilization under isothermal and non-isothermal conditions agrees with the results of our computations. However, when the depth of incorporation was limited to the upper 0.02 m, the percentages of the dosage computed to be lost by volatilization were 11 and 19%, respectively. The difference in the fraction lost by volatilization when incorporating lindane at different depths could be explained by a non-linearity in the temperature-dependence of the model parameters, e.g. the adsorption coefficient. The effect of non-linearity would decrease with depth in soil, because of the decrease in the temperature variation with depth in soil.

The magnitude of the effect of changes in soil temperature on fumigant behaviour depends on the temperature-dependence of the relevant processes in soil. The difference in sensitivity of these processes to changes in temperature is rather large. Changes in the ratio for the partitioning of fumigant between the solid and liquid phases and in the coefficient of diffusion of fumigant in air due to temperature changes are comparatively small compared with those in the ratio for the partitioning of fumigant between the liquid and gas phases and the rate coefficient of transformation. Therefore, when simulating fumigant behaviour in soil under non-isothermal conditions, there is a need for accurate data on those temperature-sensitive parameters.

12 GENERAL DISCUSSION AND CONCLUSIONS

Models describing the behaviour of fumigants in soil are based on a number of simplifications. In most models, only diffusion through the gas phase is considered in the description of fumigant transport through the soil. Other simplifications frequently used are instantaneous equilibrium in the partitioning of fumigant over the soil phases and first-order kinetics for the transformation of fumigant. In the present report, the development of such a model for the behaviour of 1,3-dichloropropene and methyl isothiocyanate (formed from metham-sodium) in the soil is described. The collection of basic data needed as input for the model is also described.

The simplified computer model for fumigant behaviour in soil can be used to obtain first estimates of the rate and extent of their emission into the air. The computations using the standard model presented in this report (Sections 7 and 9), simulating the fumigation of four fields in the northeast of the Netherlands, indicate that up to a few tens of percent of the applied dosage of fumigant can be lost by volatilization.

The results of the computations on the spreading of 1,3-dichloropropene and methyl isothiocyanate in soil were checked on a limited scale by measurements. Therefore, it is only trends that can be derived from the comparisons. In some cases, substantial differences were found between the measurements and the computations.

The measured course with time of the content profiles of fumigant in soil was not always as expected. This indicates a non-uniform injection of fumigant into the soil. Therefore, detailed measurements on the delivery of fumigant from each of the spray-nozzles, on the horizontal distribution pattern of fumigant during spraying, as well as on the variation in injection depth are needed in further studies.

During the first few days after injection of 1,3-dichloropropene into the soil of one field, the measured upward movement tended to be greater than that computed; for the soil of the other field the difference was less clear. The comparatively fast upward diffusion as measured in the field could be caused by the occurrence of large voids in the top 0.2 m layer. Such heterogeneities in soil structure were not accounted for in the standard model. A useful technique to quantify the size and number of voids could be X-ray scanning of soil cores as described by Warner et al. (1989). They obtained images showing the number, size and location of macropores (i.d. larger than 1.0 mm). Such information could be helpful in improving the modelling of fumigant behaviour in soil.

The measured contents of methyl isothiocyanate in the top 0.05 m layer were mostly lower than those computed. This difference may be explained by a comparatively high rate of transformation of the fumigant at the lower fumigant contents which occur in the soil surface layer. When a content-dependent rate of transformation was introduced into the standard model, the computed content profiles corresponded more favourably with those measured. This modification also resulted in the computation

of distinctly lower rates of emission into the air and consequently in a lower cumulative loss by volatilization.

Acceleration of the transformation of 1,3-dichloropropene after an initial period ranging from 11 to 14 days was measured in the laboratory for both soils studied. Such an acceleration was measured after 18 days for the transformation of methyl isothiocyanate in the soil of one of the fields. In the standard model, the transformation of fumigant in soils was assumed to follow first-order kinetics. Especially if accelerated transformation occurs at an early stage, the standard model may overestimate the rate and extent of emission of fumigant into the air.

In the standard model, it was assumed that local equilibrium exists between the concentrations of fumigant in the soil phases. This assumption may not be justified. On the one hand, comparatively fast diffusion can be expected through larger gas-filled voids. On the other hand, diffusion through denser soil parts with mostly water-filled pores can be expected to be very slow. Special models are needed to simulate such situations.

The loss of fumigant to the atmosphere after injection is dependent on soil and weather conditions during the fumigation period. The fumigant 1,3-dichloropropene is often injected into the soil in the first half of November. At that time of year, soils are often wet and soil temperatures comparatively low. For relatively dry soils and higher soil temperatures, more emission into the air can be expected. A higher emission, compared with that computed for the fields in this study, can also be expected when soils with low organic matter content are fumigated.

A model describing the behaviour of non-volatile pesticides in soil was modified to include vapour diffusion in the gas phase. Computations with this modified model showed that an increase in soil moisture content due to rainfall after the injection of fumigant substantially reduces the rate of its emission into the air. However, there is no simple relationship between the rate of volatilization of fumigant and soil moisture content. As the soil surface dries out (water content below a few percent), the adsorption of fumigants onto soil components strongly increases, thereby reducing their rate of emission into the air. Subsequent rewetting of the soil surface by rainfall may then result in a quick release of fumigant into the air.

Soil temperature is an important factor as it affects various processes relevant for fumigant behaviour in soil. The model describing fumigant behaviour under changing soil moisture conditions was extended by including a submodel for the variation of the temperature at the soil surface and for the transfer of heat in the soil. This enabled the effect of variation in soil temperature on the emission of fumigant into the air to be estimated. For a diurnally changing soil temperature, comparatively high rates of emission of fumigant into the air were calculated for the period around noon and comparatively low rates for the period around midnight. The cumulative emission computed for a soil system with a diurnal variation in temperature was no different from that computed for an isothermal soil system at the average temperature.

Variations in the rate of emission during the day due to changes in soil temperature can be expected to result in variations in the concentration of fumigant in the air around the fumigated field. When estimating the exposure of people living close to fumigated fields to fumigant concentrations in the air during short periods, e.g. hourly periods, substantial variations in the exposure can be expected. It should be noted that concentrations of fumigant in air above and around fumigated fields also depend on the prevailing meteorological conditions. For example, comparatively high concentrations in air can be expected during periods with low wind speed and a stable atmosphere.

The results in this report stress the need for the further development of models for fumigant behaviour in soil. Preferably, data on the input parameters should be obtained by measurements in the laboratory. To check the results of the model computations, field tests are needed including detailed measurements on the course of fumigant content in soil with position and time. On-site measurements of the rate of emission of fumigant into the air are needed to check the accuracy of the emission computed with the improved models.

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**4 SAMPLING AND ANALYSIS OF THE SOIL FUMIGANTS 1,3-DICHLORO-
PROPENE AND METHYL ISOTHIOCYANATE IN THE AIR**

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SAMPLING AND ANALYSIS OF THE SOIL FUMIGANTS 1,3-DICHLOROPROPENE AND METHYL ISOTHIOCYANATE IN THE AIR

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Abstract. Methods of sampling and analysis have been developed to measure concentrations of the soil fumigants 1,3-dichloropropene and methyl isothiocyanate (formed from metham-sodium) in air. We tested these methods under laboratory and field conditions. Air samples were taken with glass tubes containing charcoal as adsorbent. The charcoal was extracted with acetone and subsamples of the extracts were injected into a gas chromatograph with a capillary column. 1,3-dichloropropene was determined by an electron capture (EC) detector and methyl isothiocyanate by a nitrogen-phosphorus (NP) detector. Concentrations of these fumigants in 40 L of air as low as $0.2 \mu\text{g m}^{-3}$ and $1.0 \mu\text{g m}^{-3}$, respectively, could be determined. A study on the influence of storage temperature and time on the recovery from charcoal showed that charcoal tubes can be stored for up to 4 d at -20°C . A test program on the breakthrough of the charcoal tubes when sampling at different flow rates and air humidity revealed no significant breakthrough from the first to the second (check) tube. Similar results were obtained from sampling the air during fumigation of the soil in a greenhouse and in two fields.

1. Introduction

Several crops are protected against soil-borne pathogens by previous injection of 1,3-dichloropropene or metham-sodium into the soil at a depth of 0.15 to 0.20 m. In soil, metham-sodium decomposes quickly to the volatile methyl isothiocyanate. A fraction of the fumigant diffuses up to the soil surface and escapes into the air. In the discussions on the prolongation of their approval, questions arose as to the extent of emission of these fumigants to the atmosphere and regarding the possible effects of their application on the environment. Methods of sampling and analysis had to be developed to collect data on the concentration patterns around fumigated fields.

Various sorbents have been used for trapping volatile halogenated hydrocarbons in air. Parsons and Mitzner (1975) studied the trapping of 1,2-dichloroethane by Tenax (100 mg, type GC, diam. 0.25 to 0.50 mm) and measured the maximum sample volume to be greater than 1 L (flow rate below 18 L hr^{-1}). Leiber and Berk (1984) studied the use of Tenax (type GC) as adsorbent for several halogenated hydrocarbons, e.g. 1,3-dichloropropene. They used sample tubes containing 160 mg Tenax (diam. 0.18 to 0.25 mm) and back-up tubes with 40 mg Tenax. Air

samples of 10 L were taken at a rate of 12 L hr⁻¹. The amount of 1,3-dichloropropene found in the back-up tube, sampled at 50 °C at concentrations ranging from about 7 to 18 mg m⁻³, ranged from 6 to 23% of the total amount adsorbed on the Tenax in the first and the back-up tube.

Tenax (90 mg, type TA, diam. 0.5 to 0.8 mm) was tried as adsorbent at an early stage of the development of a sampling method. Although it was possible to measure concentrations of fumigant in air as low as 0.2 µg m⁻³, this method had several drawbacks (Tuinstra *et al.*, 1988). It took an hour to analyze one Tenax tube and re-injections after technical trouble were not possible. Furthermore, the storage time of Tenax tubes is limited and at higher relative humidities the volume of air that can be sampled decreases. Thus, for our research we decided not to use Tenax as adsorbent.

Charcoal tubes (100 and 50 mg sections) can be used for measuring concentrations of volatile chlorinated hydrocarbons in the range from about 1 to 1000 mg m⁻³ when sampling 10 L of air (ISO, 1985). An advantage of using charcoal tubes is that they are easy to handle in the field and in the laboratory, and no preparation of the adsorbent is needed before sampling. Saalwaechter *et al.* (1977) studied the retention of 1,1,1-trichloroethane and tetrachloroethene on charcoal tubes (BC-580-26, 100/50 mg, petroleum-based) when sampling at a rate of 60 L hr⁻¹ at 7% relative humidity with target concentrations of 2.0 and 1.0 g m⁻³, respectively. The 1% breakthrough volumes measured for these compounds were 5.8 and 33.2 L, respectively, the lower volume corresponding with the compound with the higher vapor pressure. In a protocol on the determination of chlorinated hydrocarbons in workplace air (ISO, 1985), it is noted that the breakthrough volumes for some compounds, e.g. 1,2-dichloropropane, were comparatively low when sampling for 8 hr at a rate between 1.2 and 1.8 L hr⁻¹; in such cases larger tubes (i.e. 400/200 mg) should be used.

The stability of the vapors collected on the adsorbents deserves attention. It has been noted that 1,2-dichloropropane is not stable when adsorbed on coconut-based charcoal. To remedy this problem, charcoal on petroleum basis can be used (ISO, 1985; NNI, 1985). Also, Albrecht *et al.* (1986) measured a daily loss of 7% for a 10 µg spike of 1,2-dibromo-3-chloropropane on coconut-based charcoal at 24 °C.

Little information is available on sampling methods for methyl isothiocyanate in air. Collina and Maini (1979) used tubes with charcoal (800 mg, diam. 1.5 mm) to collect this fumigant in workroom air. They sampled at a rate ranging from 120 to 240 L hr⁻¹, but gave no details on breakthrough volumes and desorption efficiency.

For the purposes of our research, the use of charcoal tubes was considered for the collection of 1,3-dichloropropene and methyl isothiocyanate in air. To determine whether this particular adsorbent was adequate to collect these fumigants in air, experiments were needed on its retention capacity under different sampling conditions. Because the sampling rate, the amount and texture of the adsorbent, as

well as the air humidity may substantially influence the retention on charcoal, tests were done in the laboratory. The stability of these fumigants collected on the charcoal needed to be checked, because the samples taken in the field may have necessitated storage for a few days before being transported to the laboratory. Furthermore, tests were set up to check the sampling and analytical methods under field conditions.

2. Materials and Methods

2.1. RETENTION OF 1,3-DICHLOROPROPENE ON CHARCOAL

The retention of 1,3-dichloropropene using charcoal tubes (SKC, 100 and 50 mg sections, petroleum-based) was tested under laboratory conditions. Petroleum-based charcoal was selected because the recovery of methyl isothiocyanate (for a spike of 0.5 μg) from charcoal on coconut basis using acetone as desorbing solvent can be low: 20% (Tuinstra *et al.*, 1988). The preparation of the test atmosphere and the loading of the charcoal tubes at 20 °C (± 0.25 °C) were done by the Netherlands Organization for Applied Scientific Research (TNO) in Apeldoorn (J. J. Akkerhuis, personal communication 1988). A constant flux of 1,3-dichloropropene into the atmosphere generator system was realized using a diffusion tube filled with this fumigant. The rate of emission from such a tube was calculated using the equation given by Parsons and Mitzner (1975). The diffusion tube was connected to a tube through which a constant air stream passed, which had been brought to the required humidity. Then, the humidified air containing the dichloropropene vapor was mixed by leading it through five air mixing compartments in series. The relative humidity of the outgoing air stream was monitored with a Vaisala, type HMI-32, whereupon air samples were taken from that stream. The total target concentration of 1,3-dichloropropene was 100 $\mu\text{g m}^{-3}$. The target concentrations of the (Z)-isomer and the (E)-isomer were 59 and 41 $\mu\text{g m}^{-3}$, respectively. All vapor samples were taken with two charcoal tubes in series; the second tube served as a check on breakthrough. A first series of samples ($n=4$) was taken to investigate the influence of sampling time, i.e. 1 and 6 hr, on the retention on charcoal when sampling 40 L of air at 60 and 90% air humidity. Further, a second series of samples ($n=6$) was taken at 60 and 90% air humidity at a flow rate ranging from 20 to 60 L hr^{-1} with a sampling time of 1 hr. The precision in the flow rate measurements was $\pm 5\%$.

A third series of vapor samples ($n=12$, including 4 duplicates) was taken in order to ascertain whether storage temperature or storage time had any influence on the amount of fumigant recovered from the charcoal. These samples were taken at a rate of 40 L hr^{-1} for 1 hr at 90% air humidity. They were stored at -20 or +20 °C for a time ranging from 1 to 14 d.

In addition, some vapor samples ($n=2$) were taken to measure the effect of a longer extraction time on the amount of fumigant recovered from the charcoal, i.e. shaking for 60 min instead of the standard 1 min. These 1-hr samples were taken at a rate of 40 L hr^{-1} at 60% air humidity.

The contents of both sections of each charcoal tube were combined and subsequently extracted with 2 mL cooled acetone by shaking for 1 min. This extraction solvent differs from that suggested by ISO (1985), i.e. carbon disulphide. The efficiency of the desorption of both fumigants from petroleum-based charcoal using the latter solvent had been found to be adequate (Tuinstra *et al.*, 1988). However, because carbon disulphide vapor is toxic and highly inflammable (ISO, 1985), safety measures need to be taken when using an autosampler in the gas chromatographic procedure. Therefore, another desorption solvent, acetone, was tried. Two methods were used to determine the desorption efficiency of acetone for 1,3-dichloropropene adsorbed on charcoal. Using the phase equilibrium method (Dommer and Melcher, 1978), 2 mL subsamples of standard solutions of 1,3-dichloropropene in acetone were shaken with 150 mg charcoal for 1 min. The amount in solution corresponded to the amount of 1,3-dichloropropene in 40 L of air at a concentration of $10 \mu\text{g m}^{-3}$. The amount left in the acetone phase was 98% ($n=15$, s.d.=2.3%). In the second method, charcoal tubes (100/50 mg) were spiked with $2 \mu\text{g}$ 1,3-dichloropropene each by injecting $10 \mu\text{L}$ of a solution of this fumigant in acetone into an air stream of 40 L hr^{-1} which was subsequently drawn through a charcoal tube. The total air volume ranged from 20 to 80 L. The contents of each section of the charcoal tubes were extracted with 1 mL cooled acetone by shaking for 1 min. Only up to 4% of the spike was found on the second section of the charcoal tube. The recovery from the first section amounted to 83% ($n=7$, s.d.=11%). When combining both sections of the charcoal tube and extracting it with 2 mL acetone, the recovery can be expected to be higher than that when extracting each section separately with 1 mL acetone. The results of the recovery experiments showed that acetone was a good alternative for carbon disulphide.

A volume of $5 \mu\text{L}$ of the 1,3-dichloropropene extracts was injected into a gas chromatograph (Perkin Elmer Sigma 2000) with a fused-silica capillary column (25 m long; 0.32 mm i.d.) coated with CP-Sil 5 CB (film thickness $1.2 \mu\text{m}$; Chrompack). The influent to the column was not split during the first 0.5 min after injection, thereafter the influent split was 1:20. The injection and detection temperatures were 250 and 300 °C, respectively. The initial temperature of the column was 45 °C and 2 min after injection it was increased at a rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ up to 100 °C, which was followed by a rate of $30 \text{ }^{\circ}\text{C min}^{-1}$ up to 220 °C. The linear flow rate of the carrier gas (He) was 15 mL min^{-1} . The fumigant was measured by electron capture (EC) with a ^{63}Ni detector. The retention times of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in this system were 6.7 and 7.0 min, respectively. The concentrations in the extracts were calculated after measuring standard solutions of 1,3-dichloropropene in acetone, with concentrations of each isomer ranging from 0.01 to $0.4 \mu\text{g mL}^{-1}$. When the concentration in the extract was greater than that in the highest standard solution, the extract was diluted. Samples from standard solutions as well as from blanks were measured regularly. The limit of detection of each isomer in 40 L of air was $0.2 \mu\text{g m}^{-3}$.

2.2. RETENTION OF METHYL ISOTHIOCYANATE ON CHARCOAL

The laboratory study on the retention of methyl isothiocyanate on charcoal (SKC, 100/50 mg, petroleum-based) was similar to that of 1,3-dichloropropene. All vapor samples were taken with two tubes in series (second tube as check) from the test atmosphere with a target concentration of $50 \mu\text{g m}^{-3}$. The contents of both sections were combined and then extracted with 2 mL cooled acetone by shaking for 1 min. Experiments similar to those for 1,3-dichloropropene were done to determine the desorption efficiency. In the phase equilibrium method, the amount of methyl isothiocyanate in acetone solution corresponded to a concentration of $10 \mu\text{g m}^{-3}$ in 40 L of air. When 150 mg charcoal was shaken with 2 mL of this solution, 70% ($n=6$, s.d.=8.8%) was left in the acetone phase. When the charcoal tubes were spiked with $2 \mu\text{g}$ methyl isothiocyanate and the contents of each section of the tubes extracted with 1 mL acetone, the amount recovered from the first section was 55% ($n=3$, s.d.=5%). Only up to 3% of the spike was found on the second section of the charcoal tube. Again, when combining both sections of the charcoal tube and extracting it with 2 mL acetone, the recovery can be expected to be higher than that when extracting each section separately with 1 mL acetone.

The fumigant was measured by gas chromatography with a nitrogen-phosphorus (NP) detector at 250°C , using the same apparatus and column as for 1,3-dichloropropene. The retention time of methyl isothiocyanate in this system was 6.6 min. The concentrations in the extracts were calculated after measuring standard solutions of methyl isothiocyanate in acetone, with concentrations ranging from 0.05 to $0.8 \mu\text{g mL}^{-1}$. When the concentration in the extract was greater than that in the highest standard solution, the extract was diluted. Samples from standard solutions as well as from blanks were measured regularly. The limit of detection when sampling 40 L of air was $1 \mu\text{g m}^{-3}$.

2.3. FIELD TEST FOR 1,3-DICHLOROPROPENE

A field test was set up to check equipment, sampling procedure and subsequent analysis. Two fields were selected: the first one near Dronten (Flevoland Province) and the second one near Noordwijkerhout (South-Holland Province). The Dronten field (8.8 ha) was injected with 150 L 1,3-dichloropropene per hectare (as Telone II) in September. The Noordwijkerhout field (1.1 ha) was injected with 275 L 1,3-dichloropropene per hectare (as Telone II), and again in September.

The air at specific sites above and around the fields was sampled with portable air sampling pumps, type Dupont P4000. The possible flow rate of these pumps can be adjusted between 20 and 4000 mL min^{-1} and the sampling rate used was checked by a flow meter. Air samples were taken with SKC charcoal tubes (100/50 mg, petroleum-based) at an air flow rate between 40 and 47 L hr^{-1} for 1 hr. All air samples were taken 1.5 m above the ground.

The samples for the Dronten field were taken on the day of injection. These air samples were taken above or downwind (30 to 100 m) of the treated field using

one charcoal tube per site. The second section of each charcoal tube was used as check section. For the Noordwijkerhout field, air samples were taken during application and one day later at sites above or on the edge of the field. Check samples were taken at an upwind distance ranging up to 100 m. To ascertain how many sampling tubes per site needed to be used, the air samples were taken with three charcoal tubes in series.

For the Dronten samples, the contents of each section of the charcoal tube were extracted with 1 mL cooled acetone. For the Noordwijkerhout samples, the contents of both sections of each charcoal tube were combined and then extracted. The analytical procedure was similar to that for the samples taken in the laboratory.

2.4. GREENHOUSE TEST FOR METHYL ISOTHIOCYANATE

A greenhouse test was set up to check the equipment, sampling procedure and subsequent analysis. The soil in the greenhouse selected (near Venlo, Limburg Province) was injected in September with 1200 L of an aqueous metham-sodium solution (510 g L^{-1}) per hectare. The soil was left uncovered after injection into the upper soil layer and the subsequent mixing of the fumigant in the soil. Shortly after application, the soil surface was sprinkled with a few mm water.

The greenhouse air was sampled with portable air sampling pumps, type Dupont P4000, during and after treatment of the soil, on the day of application and again three days later. The fumigant was sampled with SKC charcoal tubes (100/50 mg, petroleum-based) at an air flow rate between 40 and 47 L hr^{-1} for 1 hr. All air samples were taken 1.5 m above the ground. To ascertain how many sampling tubes per site needed to be used, the air samples were taken with three charcoal tubes in series.

The contents of both sections of each of the charcoal tubes were combined and then extracted. The analytical procedure was similar to that for the methyl isothiocyanate samples taken in the laboratory.

3. Results and Discussion

3.1. RETENTION OF 1,3-DICHLOROPROPENE ON CHARCOAL

The main results of the study on the influence of flow rate at different relative air humidities on the breakthrough of 1,3-dichloropropene are presented in Table I. Sampling of 1,3-dichloropropene in air for 6 hr at a flow rate of 6.7 L hr^{-1} did not result in a breakthrough. Furthermore, no breakthrough of the isomers from the first to the second charcoal tube occurred when sampling for one hour and increasing the flow rate from 20 to 60 L hr^{-1} . No influence of relative humidity (60 and 90% level) on the breakthrough of the (Z)-isomer or the (E)-isomer was measured.

The amounts of each isomer collected on the charcoal were lower than those calculated on the basis of target concentration and sample volume. The ratio of

TABLE I

Effect of flow rate and relative humidity on the breakthrough of 1,3-dichloropropene from SKC charcoal tubes

| Isomer ^a | Flow rate (L hr ⁻¹) | Relative humidity % | Mass ^b in tubes (μg) | |
|---------------------|---------------------------------|---------------------|---------------------------------|--------|
| | | | First | Second |
| Z | 20 | 60 | 0.67 | <0.01 |
| Z | 60 | 60 | 2.16 | <0.01 |
| Z | 20 | 90 | 0.63 | <0.01 |
| Z | 60 | 90 | 2.19 | <0.01 |
| E | 20 | 60 | 0.47 | <0.01 |
| E | 60 | 60 | 1.48 | <0.01 |
| E | 20 | 90 | 0.43 | <0.01 |
| E | 60 | 90 | 1.48 | <0.01 |

^a Z = (Z) - 1,3-dichloropropene.

E = (E) - 1,3-dichloropropene.

^b Not corrected for incomplete desorption.

the amount measured to be retained to that calculated was between 0.72 and 0.78 when sampling for 6 hr at 6.7 L hr⁻¹. The ratio was somewhat lower when sampling at a rate ranging from 20 to 60 L hr⁻¹: between 0.52 and 0.62. No difference in this ratio was measured between the isomers. The ratio of the (Z)-isomer to the (E)-isomer collected on the charcoal was equal to that in the gas phase: 1.47. Taking the high desorption efficiency of acetone for 1,3-dichloropropene adsorbed on charcoal into account, no explanation can be given for the comparatively low amounts measured. Presumably, the actual concentration in air was lower than the 100 μg m⁻³ intended.

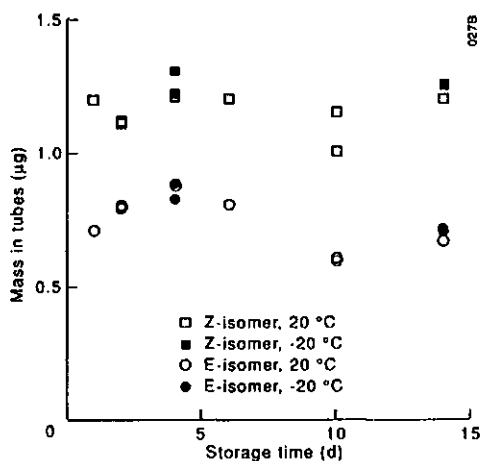


Fig. 1. Effect of storage temperature and time on the recovery of 1,3-dichloropropene from SKC charcoal tubes. Mass in tubes not corrected for incomplete desorption.

The results of the study on the influence of storage conditions on the recovery of 1,3-dichloropropene from charcoal are presented in Figure 1. When the storage time at 20 °C was increased from 1 to 14 d, the amounts recovered from the charcoal tended to be lower. At a storage temperature of -20 °C the amount of (E)-isomer recovered after 14 d was less than that after 4 d of storage. This was not measured for the (Z)-isomer. The recovery of both isomers after 4 d of storage at -20 °C was higher than after one day of storage at 20 °C. Thus, it would seem advisable that storage of the charcoal tubes loaded with 1,3-dichloropropene be restricted to less than 4 d at -20 °C.

The results of the test on the influence of extraction time on the desorption of 1,3-dichloropropene from charcoal showed no increase in the amount extracted after shaking for 1 hr with acetone when compared with that extracted after shaking for 1 min. Therefore, shaking for 1 min is sufficient for this extraction.

3.2. RETENTION OF METHYL ISOTHIOCYANATE ON CHARCOAL

The main results of the study on the influence of flow rate on the breakthrough of methyl isothiocyanate from charcoal tubes at different relative air humidities are presented in Table II. Sampling of methyl isothiocyanate in air for 6 hr at a flow rate of 6.7 L hr⁻¹ did not result in breakthrough from the first charcoal tube. Similarly, no breakthrough of methyl isothiocyanate occurred when the flow rate was increased from 20 to 60 L hr⁻¹. These results hold for both relative humidities: 60 and 90%.

The amounts of methyl isothiocyanate collected on the charcoal were lower than those calculated on the basis of target concentration and sample volume. The ratio of the amount measured to be retained to that calculated was between 0.50 and 0.58 when sampling at a flow rate of 20 L hr⁻¹. The ratio at higher flow rates was between 0.67 and 0.76. The last mentioned ratios of the amount measured to be retained to that calculated can largely be explained by the desorption efficiency of acetone for the methyl isothiocyanate adsorbed on charcoal, i.e. 70%. It is not

TABLE II
Effect of flow rate and relative humidity on the breakthrough
of methyl isothiocyanate from SKC charcoal tubes

| Flow rate (L hr ⁻¹) | Relative humidity % | Mass ^a in tubes (µg) | |
|---------------------------------------|---------------------------|---------------------------------|--------|
| | | First | Second |
| 20 | 60 | 0.50 | <0.01 |
| 60 | 60 | 2.01 | <0.01 |
| 20 | 90 | 0.58 | <0.01 |
| 60 | 90 | 2.24 | <0.01 |

^a Not corrected for incomplete desorption.

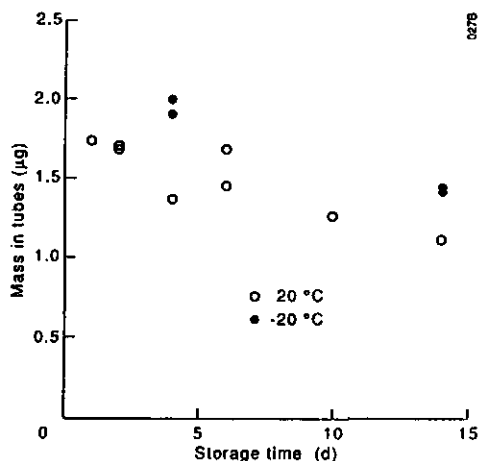


Fig. 2. Effect of storage temperature and time on the recovery of methyl isothiocyanate from SKC charcoal tubes. Mass in tubes not corrected for incomplete desorption.

clear as to what may have caused the lower ratio when sampling at a flow rate of 20 L hr^{-1} .

The results of the study on the influence of storage conditions on the recovery of methyl isothiocyanate from charcoal are presented in Figure 2. Prolonging the storage time at 20°C from 1 to 14 d resulted in a lower recovery. The amount recovered after 4 d of storage at -20°C was higher than that recovered after 1 d of storage at 20°C . Therefore it is better to store charcoal tubes loaded with methyl isothiocyanate at -20°C .

The results of the test on the influence of extraction time on the desorption of methyl isothiocyanate from charcoal showed that shaking for 1 min is sufficient.

3.3. FIELD TEST FOR 1,3-DICHLOROPROPENE

The measurements for the Dronten field showed that breakthrough from the first to the second section of the charcoal tube did not exceed 10% (first trap set at 100%). This matches the criterium set by ISO (1985) that samples are unreliable when more than 10% of the adsorbate in the front section is contained in the back-up section. On the day of application, the 1-hr concentrations of [(Z) plus (E)]-1,3-dichloropropene measured on the field ranged up to $185 \mu\text{g m}^{-3}$ (corrected for incomplete desorption). At a downwind distance of about 100 m the concentrations measured ranged up to $15 \mu\text{g m}^{-3}$.

Some results of the measurements at Noordwijkerhout for (Z)- and (E)-1,3-dichloropropene are presented in Table III. The percentage breakthrough from the first to the second tube was less than 1% for all samples.

During application, the concentrations of [(Z) plus (E)]-1,3-dichloropropene measured on the edge of the Noordwijkerhout field ranged from 5.3 to $506 \mu\text{g m}^{-3}$ (corrected for incomplete desorption). The wind direction was variable (low

TABLE III
Concentrations of (Z)- and (E)-1,3-dichloropropene in air and breakthrough from SKC charcoal tubes for the Noordwijkerhout field

| Day ^a | Retention ^b (µg) in | | | | Concentration ^b (µg m ⁻³) | |
|------------------|--------------------------------|------|----------|-------|--|-----|
| | 1st tube | | 2nd tube | | Z | E |
| | Z | E | Z | E | | |
| 0 | 3.35 | 1.05 | <0.01 | <0.01 | 78 | 25 |
| 0 | 3.70 | 2.85 | <0.01 | <0.01 | 91 | 70 |
| 1 | 11.80 | 9.05 | <0.01 | <0.01 | 274 | 210 |
| 1 | 8.65 | 7.20 | <0.01 | <0.01 | 201 | 168 |
| 1 | 5.40 | 5.00 | <0.01 | <0.01 | 116 | 108 |

^a Day 0 = day of application.

^b Corrected for incomplete desorption.

wind speed), so no clear upwind sites could be distinguished. One day later, with a southerly wind, the concentrations measured on the downwind edge of the treated field ranged from 224 to 258 µg m⁻³. As expected, low concentrations were measured on this day at sites upwind from the treated field: they were below 0.1 µg m⁻³.

3.4. GREENHOUSE TEST FOR METHYL ISOTHIOCYANATE

Some results of the test programme are presented in Table IV. The percentage breakthrough from the first to the second tube was less than 2% for all samples. No breakthrough of methyl isothiocyanate from the second to the third charcoal tube was measured.

The concentrations in greenhouse air during application and a few hours thereafter

TABLE IV
Concentrations of methyl isothiocyanate in greenhouse air and breakthrough from SKC charcoal tubes

| Day ^a | Retention ^b (µg) in | | | Concentration ^c (µg m ⁻³) |
|------------------|--------------------------------|----------|----------|--|
| | 1st tube | 2nd tube | 3rd tube | |
| 0 | 6330 | 83 | 0.7 | 143000 |
| 0 | 4390 | 8.7 | 3.7 | 94700 |
| 0 | 7080 | 87 | 13.3 | 176000 |
| 3 | 2.7 | <0.1 | <0.1 | 59 |
| 3 | 3.3 | <0.1 | <0.1 | 77 |
| 3 | 13.3 | <0.1 | <0.1 | 307 |
| 3 | 9.7 | <0.1 | <0.1 | 222 |

^a Day 0 = day of application.

^b Corrected for incomplete desorption.

^c Corrected for incomplete desorption; contents of the three tubes in series added.

ranged from 33 to 176 mg m⁻³ (corrected for incomplete desorption). On the third day after the day of application, much lower concentrations were measured: they ranged from 0.06 to 0.31 mg m⁻³.

4. General Discussion and Conclusions

The results of our study show that at air sample volumes of up to 60 L (flow rates 7 to 60 L hr⁻¹), no breakthrough of 1,3-dichloropropene from the charcoal tube (150 mg) into the second (check) tube occurred. Similar results were obtained by Albrecht *et al.* (1986), who measured no breakthrough of 1,3-dichloropropene into the check section of the charcoal tube (SKC, 100/50 mg, coconut-based), when sampling volumes in the 50 L range (sampling rate of 6 L hr⁻¹). Kring *et al.* (1984) measured more than 25% breakthrough (total trapped=100%) from charcoal tubes (SKC, 100/50 mg, petroleum-based) when sampling an 18 L sample of dichloromethane in air (relative humidity 80%; rate 3 L hr⁻¹) with vapor concentrations between 180 and 380 mg m⁻³. However, the loadings of the charcoal under these conditions are much higher than those used in our study to determine the retention of fumigant on charcoal, i.e. a few µg.

No influence of relative humidity on the retention of 1,3-dichloropropene was measured within the range of sample volumes in our study. However, according to NIOSH (1985), high air humidity during sampling may significantly decrease the retention of volatile halogenated hydrocarbons on coconut-based charcoal. In a study on the retention of 1,1,1-trichloroethane under different sampling conditions, Gregory and Elia (1983) found a 16% loss from the front section of the charcoal tube (SKC, 100/50 mg, coconut-based) to occur at humidity levels of 70% when sampling for 6 hr at a rate of 3.6 L hr⁻¹. Lower losses (3%) occurred at 10% relative humidity. It has been noted that water vapor only shows a weak competition on carbon at relative humidities below 40 to 50% (Gregory and Elia, 1983; Werner and Winters, 1986; Crittenden *et al.*, 1989). The use of smaller sample volumes and lower sampling rates could minimize possible humidity effects.

Our results indicate that vapor samples of fumigant collected on charcoal can best be stored at -20 °C and preferably for a period of not longer than 4 d. Albrecht *et al.* (1986) found that the recovery of 1,3-dichloropropene from charcoal at 24 °C did not decrease during the storage period they investigated, i.e. 12 d. However, they used coconut-based charcoal as adsorbent. Their results also show that unlike 1,2-dichloropropane, 1,3-dichloropropene is comparatively stable when adsorbed on this adsorbent. Saalwaechter *et al.* (1977) collected 5 L vapor samples of dichloromethane at a concentration of 1 mg L⁻¹ on MSA-1 coconut-based charcoal. Measurements of the contents after a period of storage of up to 57 d at 25 °C showed no loss of the adsorbate. Mann *et al.* (1980) measured a decrease from 95 to 88% in the recovery from charcoal for a spike of 0.4 µg of 1,2-dibromoethane when the storage time at ambient temperature was increased from 1 to 3 d. No loss occurred when the spiked charcoal samples were stored in the refrigerator.

The results of the retention of methyl isothiocyanate on petroleum-based charcoal when sampling at different flow rates were similar to those for 1,3-dichloropropene. No breakthrough of fumigant was measured into the second (check) tube and no influence of humidity on the retention occurred in the range of sample volumes studied (up to 60 L). Studies on the method of sampling of methyl isothiocyanate in air are scarce. No data have been found in the literature on the influence of humidity or on the effect of flow rate on the breakthrough volume when sampling methyl isothiocyanate in air.

In principle, one charcoal tube is sufficient for sampling methyl isothiocyanate and 1,3-dichloropropene in the air. However, it would seem advisable that a second charcoal tube be used as a regular check on breakthrough, especially under more extreme sampling conditions.

Acknowledgments

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**5 MEASURED AND COMPUTED CONCENTRATIONS OF METHYL
ISOTHIOCYANATE IN THE AIR AROUND FUMIGATED FIELDS**

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MEASURED AND COMPUTED CONCENTRATIONS OF METHYL ISOTHIOCYANATE IN THE AIR AROUND FUMIGATED FIELDS

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ABSTRACT

Concentrations of methyl isothiocyanate in the air around two fields were measured four to five times in a period (seven to nine days) following the injection of metham-sodium into the soil. The measured concentrations were compared with the concentrations in air computed using a gaussian plume model. During the first five days after the injection of metham-sodium into the soil of the first field, the concentrations of methyl isothiocyanate in air measured at downwind sites ranged up to about $3 \mu\text{g m}^{-3}$. After this period, they were below the detection limit of $2.0 \mu\text{g m}^{-3}$. At sites downwind from the second field, concentrations of methyl isothiocyanate in air of up to about $3 \mu\text{g m}^{-3}$ were measured one day after injection of metham-sodium. During the following six days, they were measured to range up to $1.6 \mu\text{g m}^{-3}$, and thereafter the concentrations fell below the lowered detection limit of $1.0 \mu\text{g m}^{-3}$. During the first few days after injection of metham-sodium, the computed concentrations of methyl isothiocyanate in air around the second field were lower than those measured, whereas no great differences were found for the first field. In the subsequent period, the concentrations computed for both fields tended to be higher than those measured. A better description of concentration patterns of fumigant in air requires more detailed measurements on input parameters of the dispersion model.

Keywords: air sampling, methyl isothiocyanate, volatile organic compound, pesticide, fumigant emission, field study, air quality, gaussian plume model, model evaluation

1 INTRODUCTION

Soil fumigants are regularly used in intensive arable farming to prevent the development of large populations of soil-borne pathogens. In the autumn of 1987, some 11 400 ha in an arable region in the northeast of the Netherlands were treated with metham-sodium at a rate of about 153 kg ha^{-1} . After being injected into the soil, metham-sodium is transformed into methyl isothiocyanate, largely within a day (Smelt et al., 1989), and a fraction of this volatile chemical diffuses to the surface and escapes into the air.

The environmental effects of such large-scale applications have become a major point of concern in recent years. Fumigant application does not only result in exposure of the contractors but may also lead to a certain degree of exposure of people living nearby. No value has been published yet for the maximum acceptable concentration in air, i.e. the time-weighted average concentration for exposures of up to eight hours per day, with a maximum of 40 hours per week. As the data needed for an evaluation of possible environmental effects were scarce, an air sampling programme was set up to collect data on the concentrations of methyl isothiocyanate in air around two fumigated fields.

The behaviour of metham-sodium and methyl isothiocyanate in soil can be described with a computer-simulation model. Using such a model, the rates of emission of methyl isothiocyanate into the air have been calculated for the two fields of the present study (Van den Berg and Leistra, 1992). The cumulative loss during the first three weeks, expressed as the fraction of the equivalent dosage of methyl isothiocyanate corresponding to the actual dosage of its precursor, was computed to be approximately 10% for both fields. The maximum rate of emission into the air and the time interval at which this maximum occurred were different for each field. For one field the maximum rate of emission was computed to be $1.37 \mu\text{g m}^{-2} \text{ s}^{-1}$ at 3.4 days after injection and for the other field it was $0.96 \mu\text{g m}^{-2} \text{ s}^{-1}$ at 5.8 days.

In the present study, a gaussian plume model was used to calculate the concentration patterns of methyl isothiocyanate in the air around the two fields at four to five time intervals after metham-sodium had been injected into the soil. The computed concentration patterns of methyl isothiocyanate in air are compared with the concentrations measured.

2 PROCEDURES

2.1 Application of metham-sodium and soil characteristics

The selected fields in the northeast of the Netherlands were Field A (near Valthermond) and Field B (near Eeserveen). The short SE edge of Field A borders the road along which the village of Valthermond (oriented SW-NE) is built. In other directions, there is arable land over distances of some two to three and a half kilometres. The southern long edge of Field B borders a wooded area over a length of 0.14 km. At a distance of 0.25 km, and parallel to the eastern short edge of the field, is a rural road with wind obstacles such as houses and trees. In other directions, there is arable land over a distance of about one kilometre.

The soil of Field A was treated with metham-sodium in early October 1986 and that of Field B was treated with metham-sodium at the end of September 1987. A volume of 300 l metham-sodium solution (0.51 kg l^{-1}) per ha was injected into the soil at a depth of approximately 0.18 m. The aqueous solution was injected using a horizontal-blade injector with spray nozzles below the blades, whereupon the soil surface was compressed with a roller. The injection was done strip-wise with the strips parallel to the long side of the fields. Fields A and B covered an area of 5.9 ha (0.74 by 0.08 km) and 3.4 ha (0.33 by 0.11 km), respectively.

Some characteristics of the soils of both fields were measured by a laboratory specialized in soil and crop testing (Table 1). Information on the volume fractions of the soil phases at different depths and on the physico-chemical interactions of the fumigant with the soils of the fields have been given by Van den Berg and Leistra (1992). During the first few weeks after injection of the fumigant, the average temperatures in the plough layer of Fields A and B were 12 and 11 °C, respectively.

Table 1: Characteristics of the soil of the fields treated with metham-sodium (measured by the Laboratory for Soil and Crop Testing at Oosterbeek).

| Field | pH-KCl | Organic matter content (%) | Mineral fraction (%) | |
|-------|--------|----------------------------------|----------------------|--------------------|
| | | | <2 μm | 2-50 μm |
| A | 4.3 | 13.8 | 2.5 | 7.2 |
| B | 5.2 | 6.2 | 2.2 | 6.2 |

2.2 Computation of concentration patterns of methyl isothiocyanate in the air

The concentration patterns of methyl isothiocyanate in the air around the fumigated fields were calculated with the PAL (Point-Area-Line) model, which is based on the gaussian plume concept. The PAL model was developed by the US Environmental Protection Agency and it describes the short-term dispersion of chemicals in air (Petersen, 1978). In a gaussian plume model, it is assumed that dispersion from point, area and line sources results in gaussian distributions in both the lateral and vertical directions through the plume dispersing from that source.

A modified set of dispersion coefficients was introduced as recommended by the TNO Working Group "Dispersion Air Pollutants" (1981 and 1984) to be used for ground level sources. The dispersion coefficients of this set also depend on the roughness length of the earth's surface. In the present calculations, the value of the roughness length was taken to be 0.05 m, which is assumed to correspond to the surface roughness in the northeastern part of the Netherlands, where the selected fields are situated.

The input data for the area sources representing the fumigated fields consisted of their size (km) and orientation, source strength ($\text{g m}^{-2} \text{s}^{-1}$) and source height (m). Hourly values of the rate of emission of the fumigant from the fields into the air, as derived from computations by Van den Berg and Leistra (1992), were taken as the source strength. In view of the simplified description of fumigant behaviour in soil as used in the model of Van den Berg and Leistra (1992), the computed rates of emission of methyl isothiocyanate into the air should be considered as first estimates. The source height was taken to be 0 m.

Meteorological data required by the PAL model involve wind speed (m s^{-1}), wind direction (degrees), atmospheric stability (Pasquill stability class) and mixing height (m). The data on wind speed and wind direction at a height of 2.0 m were obtained from measurements done with a Woelfle anemometer installed in the fields studied. Data on the atmospheric stability condition were obtained from the weather station of the Royal Netherlands Meteorological Institute at Eelde airport (Province of Drenthe). It was assumed that the stability condition of the atmosphere at the locations of the fields was the same as that for Eelde airport. The distances between this airport and Fields A and B were 35 and 30 km, respectively. The mixing height to be introduced into the model depends on the stability condition of the atmosphere; its value usually has little effect if distances between source and receptor are small (Petersen, 1978). The values of the mixing height were taken from the TNO Working Group "Dispersion Air Pollutants" (1984). The input data for the PAL model to simulate the field situations are presented in Tables 2 and 3.

Concentration patterns in the air around Field A were computed for a rectangular area of 1.5 km^2 and those around Field B were computed for a square area of 1.0 km^2 . By rotation, the field sides had to be placed parallel to the axes of the co-ordinate system of the model. The wind direction was rotated in the same way, to be introduced also relative to this co-ordinate system. The hourly concentrations in air were calculated at the grid-points of a grid with a grid-line distance of 0.1 km.

Table 2: Input data for the PAL model used to calculate the dispersion of methyl isothiocyanate in air at four intervals after injection of metham-sodium into the soil of Field A.

| Interval after Injection (days) | Rate of emission* ($\mu\text{g m}^{-2} \text{s}^{-1}$) | Wind speed (m s^{-1}) | Wind direction (degrees) | Stability class (Pasquill) | Mixing height (m) |
|---------------------------------|--|----------------------------------|--------------------------|----------------------------|-------------------|
| 1.9 | 0.80 | 3.4 | 268 | B | 1500 |
| 2.9 | 1.30 | 6.2 | 38 | C | 1000 |
| 5.0 | 1.10 | 2.5 | 108 | D | 500 |
| 6.9 | 0.79 | 6.3 | 338 | B | 1500 |

* In PAL model expressed as $\text{g m}^{-2} \text{s}^{-1}$.

Table 3: Input data for the PAL model used to calculate the dispersion of methyl isothiocyanate in air at five intervals after injection of metham-sodium into the soil of Field B.

| Interval after Injection (days) | Rate of emission* ($\mu\text{g m}^{-2} \text{s}^{-1}$) | Wind speed (m s^{-1}) | Wind direction (degrees) | Stability class (Pasquill) | Mixing height (m) |
|---------------------------------|--|----------------------------------|--------------------------|----------------------------|-------------------|
| 1.1 | 0.03 | 6.3 | 80 | C | 1000 |
| 3.1 | 0.53 | 4.3 | 115 | B | 1500 |
| 5.2 | 0.95 | 5.3 | 160 | D | 500 |
| 6.9 | 0.92 | 2.7 | 250 | B | 1500 |
| 9.1 | 0.77 | 6.5 | 295 | C | 1000 |

* In PAL model expressed as $\text{g m}^{-2} \text{s}^{-1}$.

The height for which the concentrations in air were calculated was 1.5 m, the same as the height at which the air samples were taken in the field. A FORTRAN computer program using graphical sub-routines (UNIRAS, 1985 and 1986) was made to present the results of each run in figures with concentration patterns. The concentration class boundaries were set at 0.2, 1.0, 5.0, 10.0 and $20 \mu\text{g m}^{-3}$.

2.3 Measurement of methyl isothiocyanate in the air

The air was sampled with charcoal tubes (SKC, 100/50 mg, petroleum-based) using portable sampling pumps, type Dupont P4000 or P4LC. Each pump contains a flow control unit, which maintains the flow rate at $\pm 5\%$. Air samples of approximately 40 litres were taken (at a rate of approximately 40 l h^{-1}) with two charcoal tubes in series per site. The second charcoal tube was used as a check on breakthrough of the fumigant from the first tube. Van den Berg et al. (1992a) have shown that no breakthrough occurs when sampling air volumes up to 60 litres (at a rate of 60 l h^{-1}). On each sampling day, the air samples were taken 1.5 m above the soil surface at

a series of sampling points (most times in line with each other), which generally consisted of one or two air samples taken upwind of the treated field (at an upwind distance ranging from 0 to 50 m) and of four to six air samples taken at sites downwind of the treated field. The charcoal tubes were stored in a cooling box at a temperature of a few degrees celsius or in a deep-freeze for up to about two days before they could be transported to the laboratory, where they were kept in a deep-freeze until analysis. As the charcoal tubes in this study were only stored for a few days before extraction, no significant decrease in the recovery of methyl isothiocyanate from charcoal occurred (Van den Berg et al., 1992a).

For analysis of the samples, the contents of both sections of each charcoal tube were first combined and then extracted with 2 ml cooled acetone. A sub-sample of 5 μ l was injected into a gas chromatograph (Perkin Elmer Sigma 2000) with a fused-silica capillary column (25 m long; 0.32 mm i.d.) coated with CP-Sil 5 CB (film thickness 1.2 μ m; Chrompack). The fumigant was determined by a nitrogen-phosphorus (NP) detector. The concentrations of fumigant in the extracts were calculated after measuring standard solutions of fumigant in acetone. More details on the analytical procedure have been given by Van den Berg et al. (1992a). The desorption efficiency of acetone for methyl isothiocyanate adsorbed on charcoal at a load corresponding to the amount of this fumigant in 40 l of air at a concentration of 10 μ g m⁻³, as determined by the phase equilibrium method, was 70% (n=6, s.d.= 9%). For the 1986 measurements (Field A), the limit of detection of methyl isothiocyanate in 40 l of air was 2.0 μ g m⁻³. During the next year, the analytical procedure was improved which resulted in a lowering of the detection limit to 1.0 μ g m⁻³ for the 1987 measurements (Field B).

3 RESULTS AND DISCUSSION

3.1 Computations and measurements for Field A

The results of the computations on the dispersion of methyl isothiocyanate in air around the fumigated fields are represented in figures with isoconcentration lines for a height of 1.5 m. In these figures, the smaller numbers represent the concentrations measured at the same height and they are placed next to the measurement sites (indicated by triangles).

The pattern of concentrations of methyl isothiocyanate in air at an interval of 1.9 days after injecting metham-sodium into the soil of Field A is presented in Figure 1 (left-hand side). The concentration measured at a downwind distance of about 180 m was $3.1 \mu\text{g m}^{-3}$, whereas the $1.0 \mu\text{g m}^{-3}$ isoconcentration line was calculated to be at about a distance of 140 m from the downwind edge of the field. A field bordering the SW long edge of Field A and similar in size, which was injected with metham-sodium one day after Field A had been injected, may have contributed to this concentration. During the sampling period, the air also passed over that adjacent field.

The pattern of concentrations computed for 2.9 days after injection is presented in Figure 1 (right-hand side). Concentrations of methyl isothiocyanate in the air at the downwind edge of the field of up to $3.9 \mu\text{g m}^{-3}$ were computed, which is somewhat higher than the concentration measured: $2.7 \mu\text{g m}^{-3}$. Upwind of Field A, concentrations of $3.1 \mu\text{g m}^{-3}$ were measured, which can be explained from the position of these sampling sites above the previously mentioned adjacent fumigated field.

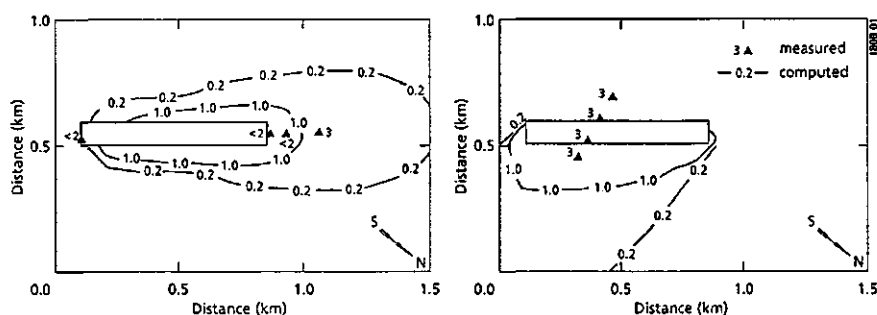


Fig. 1: Pattern of concentrations ($\mu\text{g m}^{-3}$) of methyl isothiocyanate in the air at a height of 1.5 m computed for Field A at 1.9 (left-hand side) and 2.9 (right-hand side) days after injection of metham-sodium into the soil. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

Presumably, this field contributed to the concentrations downwind of Field A. Because of the higher source strength and the less unstable atmosphere as introduced in the PAL model for 2.9 days (See Table 2), the concentration in air would be expected to be higher than after 1.9 days. However, these effects are counteracted by a higher wind speed and by the wind direction not being parallel to the long edge of the fumigated field. At 2.9 days, the source strength was computed to be close to its maximum, i.e. $1.37 \mu\text{g m}^{-2} \text{s}^{-1}$ at 3.4 days after injection of metham-sodium into the soil (Van den Berg and Leistra, 1992; See Table 2).

The pattern of concentrations at 5.0 days after injection is presented in Figure 2 (left-hand side). The concentrations measured were lower than those calculated: at the downwind edge of the field concentrations of up to $14 \mu\text{g m}^{-3}$ were calculated, whereas the concentration measured was only $2.1 \mu\text{g m}^{-3}$. At a distance 150 m further downwind, the concentration measured was $2.9 \mu\text{g m}^{-3}$. Although the computed rate of emission at this time interval was somewhat lower than at the previous interval, the lower wind speed and the less unstable atmosphere, compared with the conditions introduced in the PAL model for a time interval of 2.9 days (See Table 2), resulted in less dispersion of the fumigant in air and therefore higher concentrations were calculated. Because of the wind direction at the time of sampling, wind obstacles such as trees and houses were then situated close to the sampling sites downwind of the field. This may have lowered the concentrations in air, because such obstacles disturb the wind field and can be expected to increase the turbulent mixing of the air. By neglecting such effects in the PAL model, the computations will tend to overestimate fumigant concentrations in air.

The pattern of concentrations at 6.9 days after injection is presented in Figure 2 (right-hand side). The concentrations calculated at the downwind edge of the field were $1.8 \mu\text{g m}^{-3}$ or less, whereas those measured remained below the detection limit

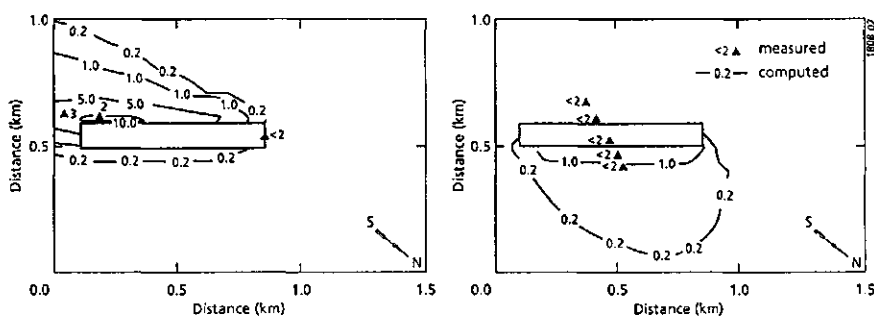


Fig. 2: Pattern of concentrations ($\mu\text{g m}^{-3}$) of methyl isothiocyanate in the air at a height of 1.5 m computed for Field A at 5.0 (left-hand side) and 6.9 (right-hand side) days after injection of metham-sodium into the soil. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

of $2.0 \mu\text{g m}^{-3}$. For the next one-hour period, the concentrations computed at the downwind edge ranged up to $2.4 \mu\text{g m}^{-3}$. Again, the concentrations measured during that period remained below the detection limit. At 6.9 days, the computed source strength had decreased to 58% of its maximum (See Table 2). Further, the higher wind speed and the more unstable atmosphere as introduced in the model also contributed to the lower concentrations computed, compared with those computed for the preceding two intervals.

The concentrations of methyl isothiocyanate in air computed for the sites downwind of Field A where air samples were taken, as well as the concentrations measured at those sites, are summarized in Table 4. As the downwind concentration in air computed with the PAL model is proportional to the source strength, the course of the computed downwind concentrations of methyl isothiocyanate in air with time would be expected to follow that of the rate of emission of this fumigant into the air as introduced in the PAL model. However, the effect of a change in the source strength can be counteracted by changing meteorological conditions. As a consequence, the course of the computed concentrations of methyl isothiocyanate in air downwind of Field A only roughly followed that of the rate of emission.

The computed and measured concentrations were of the same order of magnitude during the first few days after injection (Table 4). At 5.0 days, the computed concentrations were distinctly higher than those measured.

Table 4: Computed and measured concentrations of methyl isothiocyanate in the air downwind of Field A after its injection with metham-sodium.

| Time after injection (d) | Downwind distance (m) | Concentration in air ($\mu\text{g m}^{-3}$) | |
|-----------------------------|--------------------------|---|----------|
| | | computed | measured |
| 1.9 | 0 | 4.7 | < 2.0 |
| 1.9 | 51 | 2.4 | < 2.0 |
| 1.9 | 192 | 0.8 | 3.1 |
| 2.9 | 0 | 3.9 | 2.7 |
| 2.9 | 55 | 2.0 | 2.6 |
| 5.0 | 0 | 14.0 | 2.1 |
| 5.0 | 150 | 8.2 | 2.9 |
| 6.9 | 0 | 1.8 | < 2.0 |
| 6.9 | 51 | 1.0 | < 2.0 |
| 6.9 | 99 | 0.7 | < 2.0 |

Some additional computations were done to estimate the effect of the previously mentioned fumigated field SW of Field A on the concentrations in air downwind of Field A. It was assumed that the course of the source strength of the emission from that field with time after its injection with metham-sodium was the same as that for Field A. At 1.9 days after injection of Field A, the contribution of the neighbouring field was negligible, which can be explained by the combination of a low source strength of the emission from that field and the prevailing wind direction. At 2.9 days after injection of Field A, the emission from the neighbouring field was computed to increase the concentration of fumigant on the downwind edge of Field A by about 30%. At 5.0 days after injection of Field A, there was little influence of the neighbouring field, which can be explained by the wind direction. At 6.9 days after injection of Field A, the increase in the concentration on the downwind edge of Field A due to the neighbouring field was computed to be about 45%.

3.2 Computations and measurements for Field B

At an interval of 1.1 day after injecting metham-sodium into the soil of Field B, the concentrations of methyl isothiocyanate measured in air at downwind distances of 0, 50, 90, 130 and 170 m were 1.8, 3.1, 1.1, 1.0 and below $1.0 \mu\text{g m}^{-3}$, respectively. The computed concentrations in air were in the lowest concentration class, i.e. below $0.2 \mu\text{g m}^{-3}$. This difference between the concentrations computed and those measured indicates that the actual source strength of methyl isothiocyanate at this time was higher than that computed. Concentrations between 1.2 and $1.3 \mu\text{g m}^{-3}$ were measured close to the upwind long edge of the field. As the wind direction was almost parallel to the long edge of the field, small fluctuations in this direction may have resulted in a contribution of vapour released from the field.

The pattern of concentrations of methyl isothiocyanate in air at an interval of 3.1 days after injection is presented in Figure 3 (left-hand side). The concentrations computed at the downwind edge of the field were around $2.5 \mu\text{g m}^{-3}$. The concentrations measured at this time interval were lower: they remained below the detection limit of $1.0 \mu\text{g m}^{-3}$. The higher concentrations computed, compared with those at an interval of 1.1 days, can be ascribed to the lower wind speed and the higher source strength as introduced in the model (See Table 3).

The pattern of concentrations at an interval of 5.2 days after injection is presented in Figure 3 (right-hand side). The computed concentrations of methyl isothiocyanate in air at the downwind edge of the field ranged from 3.0 to $3.8 \mu\text{g m}^{-3}$. The concentrations measured downwind were somewhat lower than those computed: they decreased from $1.6 \mu\text{g m}^{-3}$ at the downwind edge to below $1.0 \mu\text{g m}^{-3}$ at a distance 75 m further downwind. At this time interval, the source strength was computed to be almost at its maximum, i.e. $0.96 \mu\text{g m}^{-2} \text{s}^{-1}$ at 5.8 days after injection of metham-sodium into the soil (Van den Berg and Leistra, 1992). However, the effect of this comparatively high source strength, compared with that computed for an interval of 3.1 days, is counteracted by the higher wind speed (Table 3) and by the wind direction being almost perpendicular to the long edge of the field.

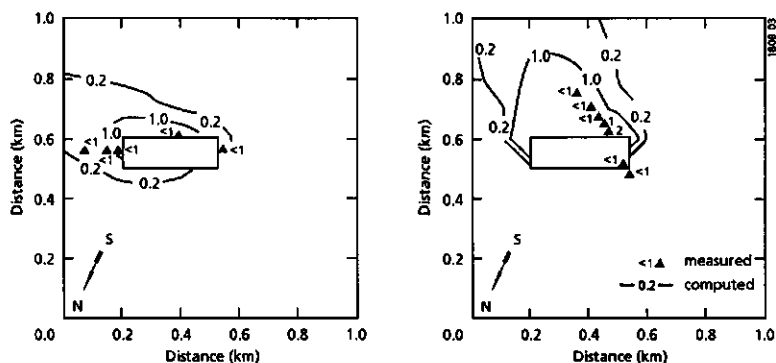


Fig. 3: Pattern of concentrations ($\mu\text{g m}^{-3}$) of methyl isothiocyanate in the air at a height of 1.5 m computed for Field B at 3.1 (left-hand side) and 5.2 (right-hand side) days after injection of metham-sodium into the soil. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

The pattern of concentrations at an interval of 6.9 days after injection is presented in Figure 4 (left-hand side). The computed concentrations of fumigant on the downwind edge ranged up to $6.5 \mu\text{g m}^{-3}$. The concentrations measured in the field were lower than those computed: they were $1.3 \mu\text{g m}^{-3}$ or less; this latter concentration was measured at a downwind distance of about 35 m. Although wind speed was fairly low, i.e. 2.7 m s^{-1} , concentrations considerably higher than $1.0 \mu\text{g m}^{-3}$ did not occur. Although the source strength at 6.9 days, as introduced in the PAL model, was slightly lower than that of about two days earlier (Table 3), the computed

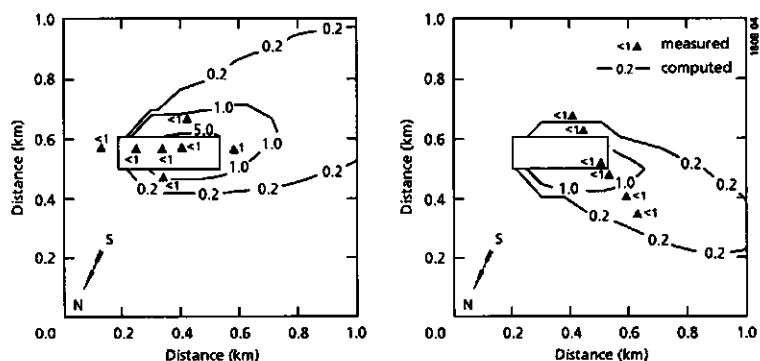


Fig. 4: Pattern of concentrations ($\mu\text{g m}^{-3}$) of methyl isothiocyanate in the air at a height of 1.5 m computed for Field B at 6.9 (left-hand side) and 9.1 (right-hand side) days after injection of metham-sodium into the soil. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

concentrations in air were higher. This can be explained by the lower wind speed and by the wind direction being almost parallel to the long edge of the field.

The pattern of concentrations at an interval of 9.1 days after injection is presented in Figure 4 (right-hand side). The computed concentrations at the downwind edge of the field ranged up to about $3.0 \mu\text{g m}^{-3}$, whereas those measured downwind from the field were lower: they remained below the detection limit of $1.0 \mu\text{g m}^{-3}$. At this time interval after injection, the computed source strength had decreased to 80% of its maximum (Table 3). The lower concentrations computed for the downwind edge, compared with those computed for 6.9 days after injection, can be explained by the lower source strength and the higher wind speed, although the effect of these factors is somewhat counterbalanced by the less unstable atmosphere at 9.1 days after injection than at 6.9 days.

The concentrations of methyl isothiocyanate in air computed for the sites downwind of Field B where air samples were taken, as well as the concentrations measured at those sites, are summarized in Table 5. At 1.1 days after injection, the computed concentrations were much lower than those measured. At 5.2 days and later, the computed concentrations were higher than those measured.

Table 5: Computed and measured concentrations of methyl isothiocyanate in the air downwind of Field B after its injection with metham-sodium.

| Time after injection (d) | Downwind distance (m) | Concentration in air ($\mu\text{g m}^{-3}$) | |
|-----------------------------|--------------------------|---|----------|
| | | computed | measured |
| 1.1 | 0 | 0.1 | 1.8 |
| 1.1 | 50 | 0.1 | 3.1 |
| 1.1 | 90 | 0.1 | 1.1 |
| 1.1 | 130 | 0.0 | 1.0 |
| 1.1 | 170 | 0.0 | < 1.0 |
| 3.1 | 0 | 2.1 | < 1.0 |
| 3.1 | 45 | 0.9 | < 1.0 |
| 3.1 | 125 | 0.3 | < 1.0 |
| 5.2 | 0 | 3.9 | 1.6 |
| 5.2 | 40 | 3.2 | 1.2 |
| 5.2 | 74 | 2.5 | < 1.0 |
| 5.2 | 111 | 2.1 | < 1.0 |
| 5.2 | 178 | 1.6 | < 1.0 |
| 6.9 | 36 | 3.6 | 1.3 |
| 9.1 | 0 | 3.0 | < 1.0 |
| 9.1 | 47 | 1.4 | < 1.0 |
| 9.1 | 82 | 1.0 | < 1.0 |
| 9.1 | 130 | 0.6 | < 1.0 |
| 9.1 | 214 | 0.4 | < 1.0 |

4 GENERAL DISCUSSION AND CONCLUSIONS

In the period from about three days after injection into the soil of Field A, the computed concentrations in air tended to be higher than those measured. This difference may have been caused by an overestimation of the source strength of emission of methyl isothiocyanate from the soil into the air. Van den Berg and Leistra (1992) discussed the difficulties when simulating the behaviour of methyl isothiocyanate in soil, in particular with respect to the description of its transformation in soil. The transformation is comparatively fast at low fumigant contents, so the rate of transformation in the layer near the soil surface may have been underestimated, which results in an overestimation of the rate of emission into the air.

At about one day after injection of metham-sodium into the soil of Field B, the computed downwind concentrations of methyl isothiocyanate in air were lower than those measured. Presumably, the actual source strength at that time was higher than that computed, which may have been caused by the presence of large voids in the top 0.20 m layer or by a locally shallower depth of injection. Both factors would result in a faster diffusion of the fumigant to the soil surface and they were not accounted for in the computer-simulation model used by Van den Berg and Leistra (1992) to calculate the rate of emission into the air. For the period from about three days after injection onwards, the computed concentrations were higher than those measured and this may have been caused by an overestimation of the rate of emission into the air by the same cause as mentioned for Field A.

In this study, the one-hour concentrations of methyl isothiocyanate in air measured around the fields on the days following the day of injection of metham-sodium into the soil ranged up to a few $\mu\text{g m}^{-3}$. So far, data have not been published to evaluate whether such concentrations have adverse effects on human health. Information on both the short-term and long-term toxicological effects of methyl isothiocyanate in air is needed. Comparatively high concentrations of fumigant in air have been measured during application (Van den Berg et al., 1992a), both in the field and in a greenhouse. Consequently, it may be necessary to minimize exposure of contractors to methyl isothiocyanate in air on the day of application by improving application techniques.

Uncertainties in the source strength make it rather difficult to validate the model for vapour dispersion in air, thus stressing the need for measurements of the source strength instead of making estimates. This is illustrated by the study of Chitgopekar et al. (1990), who introduced estimated values of the source strength into a gaussian plume type model when computing the spread in air of chloro-ethene emitted from a waste disposal site. They found substantial differences between the concentrations measured and those computed for one of the two periods during which air samples were taken.

An important factor when calculating the dispersion of fumigants in the air is the stability condition of the air above and around the fumigated fields during the simulated periods. A change in stability requires other values of the dispersion parameters to be used in the gaussian plume model, which affects the concentrations computed with the model substantially (Janni, 1982; Van den Berg et al., 1992b). In the present study, the stability condition of the surface air layer was taken to be the same as that measured at a nearby weather station, at a distance of some 30 km from the fumigated fields. However, a different stability condition may have occurred, for example due to differences in the rate of breakdown of a night-time inversion layer. Measurement of the stability condition of the surface air layer at the location of the field studied would have eliminated this uncertainty. A relatively simple method of determining the Pasquill stability class from cloud cover and wind speed has been described by Wieringa (1973). The Pasquill stability class may also be determined from the Monin-Obukhov length, L , and the roughness length for the terrain (Golder, 1972). A value of L can be obtained using the profile method described by Van Ulden and Holtslag (1985), which requires the measurement of the wind speed at a single height above the soil surface and the air temperature at two heights, for example at 2 and 10 m.

It should be noted that in the PAL model a level terrain is assumed. Although the region in the northeast of the Netherlands where Fields A and B are located is flat, there are wind obstacles such as houses and trees. In this dispersion model, the presence of such obstacles is accounted for in the value for the roughness length. However, on a local scale, the obstacles present in the neighbourhood of the fields studied may have affected the pattern of concentrations of fumigant in air more strongly than was accounted for in the model. The influence of obstacles depends on their position relative to the sampling sites. The assessment of the influence of obstacles on dispersion on a local scale is an interesting topic for further research.

Although a gaussian plume model has several limitations, for example the dispersion in the vertical direction is mostly non-gaussian (Gryning et al., 1987), the results of the use of the gaussian plume model in this study are encouraging. Further improvements in the description of the patterns of concentrations of fumigant in air around treated fields seem possible. In the first place, the quality of input data on the source strength and on the stability condition of the surface air layer can be improved by on-site measurements. Secondly, improvement of the set of dispersion coefficients in the gaussian plume model may be possible, because in the present model average values of the dispersion coefficients were used for each stability class. Detailed measurements around fumigated fields are needed to check the effect of possible improvements on the description of the patterns of concentrations in air as computed with the dispersion model.

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**6 MEASURED AND COMPUTED CONCENTRATIONS OF 1,3-DICHLORO-
PROPENE IN THE AIR AROUND FUMIGATED FIELDS**

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MEASURED AND COMPUTED CONCENTRATIONS OF 1,3-DICHLOROPROPENE IN THE AIR AROUND FUMIGATED FIELDS

Running title: concentrations of 1,3-dichloropropene in air

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ABSTRACT

Concentration patterns of both isomers of 1,3-dichloropropene in air around two fields were computed with a gaussian plume model for six time intervals after injection of the fumigant into the soil and they were compared with the concentrations measured in the air. During the first three days after the injection of 1,3-dichloropropene into the soil of one field, the downwind concentrations of 1,3-dichloropropene in air computed for a height of 1.5 m above the ground ranged up to $19 \mu\text{g m}^{-3}$, whereas the downwind concentrations measured ranged up to $29 \mu\text{g m}^{-3}$. For the period from five to ten days after injection, the concentrations computed and those measured ranged up to $36 \mu\text{g m}^{-3}$ and $16 \mu\text{g m}^{-3}$, respectively. For the other field, the computed downwind concentrations in air ranged up to $0.6 \mu\text{g m}^{-3}$ during the first three days after injection, whereas those measured ranged up to $23 \mu\text{g m}^{-3}$. For the period from four to nine days after injection, the concentrations computed and those measured ranged up to 2.3 and $1.3 \mu\text{g m}^{-3}$, respectively. The computations under-estimated the concentrations in air during the first three days following application, but on later days the computed and measured concentrations were mostly at the same level.

1 INTRODUCTION

Soil fumigants are regularly used in intensive farming to prevent the development of large populations of soil-borne pathogens. In the autumn of 1987, some 3 700 ha in the arable region of the northeast of the Netherlands were treated with 1,3-dichloropropene at a rate of about 150 l ha⁻¹. After being injected into the soil, a fraction of this volatile chemical diffuses up to the surface and escapes into the air.

The environmental effects of such large-scale applications have become a major point of concern in recent years. Fumigant application does not only result in exposure of contractors but may also lead to a certain degree of exposure of people living nearby. In the Netherlands, the maximum acceptable concentration of 1,3-dichloropropene in air, as a time-weighted average for exposures of up to 8 h per day with a maximum of 40 h per week, amounts to 5 mg m⁻³.¹ This concentration is equal to the Threshold Limit Value (time-weighted average) as adopted by the American Conference of Governmental Industrial Hygienists.² Exposures to concentrations of 5 mg m⁻³ have been measured during fumigation practices in pineapple plantations for workers standing on a metal grate platform directly above the fumigation shanks, but in general concentrations to which employees were exposed were lower.³ In the Netherlands, no limit value has been established as yet for the exposure of the population. As little information was available about concentrations of 1,3-dichloropropene in air near sites of application of this fumigant in the Netherlands, an air sampling programme was set up to collect data on concentrations of this fumigant in air around two fumigated fields. Air samples were taken at several time intervals after the fields had been injected with 1,3-dichloropropene.

The behaviour of 1,3-dichloropropene in soil can be described using a computer-simulation model. Using such a model, Leistra and Frissel⁴ calculated that up to about 50% of the dosage of the more volatile (Z)-isomer may enter the atmosphere after its injection into the soil at a depth between 0.15 and 0.20 m. For the two fields of the present study, the rates of emission of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene into the air following injection into the soil have been computed.⁵ During the first day after injection the rates of emission increased only slowly. After that, the rate of emission of the (Z)-isomer increased more rapidly and reached maximum values of 0.72 µg m⁻² s⁻¹ at 11 days after injection of one field and of 2.1 µg m⁻² s⁻¹ at 6 days after injection of the other field. The corresponding maximum rates of emission of the (E)-isomer for these fields were computed to be 0.28 µg m⁻² s⁻¹ at 18 days after injection and 0.79 µg m⁻² s⁻¹ at 9 days after injection. The maximum rate of emission of the (E)-isomer from a fumigated field was computed to be lower than that of the (Z)-isomer and it occurred later, which is due to the lower volatility of the (E)-isomer. Three weeks after injection the differences between the computed rates of emission of both isomers were small for both fields. The rate was about 0.4 µg m⁻² s⁻¹ for the (Z)-isomer and about 0.3 µg m⁻² s⁻¹ for the (E)-isomer. The cumulative loss by volatilization in the first three weeks after injection was

calculated to range from 9.5 to 22% of the dosage of the (Z)-isomer and from 3.7 to 12% of that of the (E)-isomer.

In this study, a gaussian plume model was used to compute the patterns of concentration of 1,3-dichloropropene in air around the two fields at several time intervals after they had been injected with this fumigant. The computed concentration patterns are compared with the concentrations measured in the air.

2 PROCEDURES

2.1 Application of 1,3-dichloropropene and soil characteristics

The selected fields in the northeast of the Netherlands were Field A and Field B, which are both located near Valthermond (Province of Drenthe). This village is built along two parallel roads (about 8 km long), which are oriented NE-SW. To the northwest and the southeast, there is arable land over distances of at least two kilometres. The SE short edge of Field A borders the northern road through Valthermond. The NW short edge of Field B is parallel to the southern road. The distance between that edge and the southern road is about 0.17 km. Fields A and B were treated with 1,3-dichloropropene on October 28, 1987 (from 7.35 until 11.25 h Central European Time) and on November 7, 1987 (from 10.20 until 16.35 h Central European Time), respectively. The dosage of Telone II (> 92% 1,3-dichloropropene) was 150 litres per hectare for both fields. This product contains a mixture of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in a ratio of about 1.2.

The fumigant was injected at a depth between 0.15 and 0.20 m using a horizontal-blade type injector with spray nozzles under the blades. After the injection of the fumigant into the soil, the soil surface was pressed with a roller. The injection was done strip-wise with the strips parallel to the long side of the field. Fields A and B cover an area of 5.1 ha (0.63 by 0.08 km) and 6.2 ha (0.76 by 0.08 km), respectively.

Some characteristics of the top 0.2 m layer of the two fields studied were measured by a laboratory specialized in Soil and Crop Testing and they are presented in Table 1. Information on the volume fractions of the soil phases at different depths and on the parameters characterizing the physico-chemical interactions of the fumigant with the soils of the fields were presented by Van den Berg and Leistra.⁵ During the first few weeks after injection, the average temperatures of the plough layer of Fields A and B were 9 and 6 °C, respectively.

Table 1: Characteristics of the soils of the fields treated with 1,3-dichloropropene (measured by the Laboratory for Soil and Crop Testing at Oosterbeek).

| Field | pH-KCl | Organic matter content (%) | Mineral fraction (%) | |
|-------|--------|----------------------------------|----------------------|---------|
| | | | <2 µm | 2-50 µm |
| A | 5.1 | 15.7 | 2.7 | 7.3 |
| B | 5.4 | 24.6 | 0.3 | 1.3 |

2.2 Computation of concentration patterns of 1,3-dichloropropene in the air

The patterns of concentrations of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in air around the fumigated fields were calculated with the PAL (Point-Area-Line) model, which is a gaussian plume type model developed by the U.S. Environmental Protection Agency (EPA) for the short-term dispersion of gaseous compounds in air.⁶

A modified set of dispersion coefficients was introduced into the PAL model, according to recommendations by the TNO Working Group "Dispersion Air Pollutants".^{7,8} This set has been recommended to be used in the gaussian plume model when computing the dispersion of air pollutants from ground level sources. The dispersion coefficients of this set depend on the roughness length, which characterizes the roughness of the soil - air interface. The value of this parameter depends on the number, the type and the size of roughness elements in the area studied. In the present calculations, the roughness length was taken to be 0.05 m, which is assumed to correspond to the roughness of the soil surface of the arable land in the northeast of the Netherlands.

The input data for the area sources representing the fumigated fields consisted of their size (km) and orientation, source strength ($\text{g m}^{-2} \text{s}^{-1}$) and source height (m). Hourly values of the rate of emission for each isomer into the air, as derived from the computations by Van den Berg and Leistra,⁵ were taken as the source strength. The starting time of the fumigation was set half-way through the actual period of injection for both fields. The source height was taken to be 0 m.

Meteorological data required by the PAL model involve hourly values of wind speed (m s^{-1}), wind direction (degrees), atmospheric stability (Pasquill stability class) and mixing height (m). The data on wind speed and wind direction at a height of 2.0 m were obtained from measurements done with a Woelfle anemometer installed in the fields studied. Data on the atmospheric stability condition were obtained from the weather station of the Royal Netherlands Meteorological Institute at Eelde airport (Province of Drenthe). It was assumed that the stability condition of the surface air layer at the locations of the fields studied was the same as that for Eelde airport. The distance between both fields and Eelde airport was about 35 km. The mixing height depends on the stability condition of the atmosphere, and its value usually has little effect on downwind concentrations if the distances between source and receptor are small.⁶ The values of the mixing height were taken from the TNO Working Group "Dispersion Air Pollutants".⁸ The input data for the PAL model for the simulation of the field situations are presented in Tables 2 and 3.

Concentration patterns of fumigant in the air around the fields were computed for a square area of 1.0 km^2 . By rotation, the field sides had to be placed parallel to the axes of the co-ordinate system of the model. The wind direction was rotated in the same way, to be introduced also relative to this co-ordinate system. The hourly concentrations were calculated at the grid-points of a grid with a grid-line distance of 0.1 km. Separate runs were done for the (Z)-isomer and the (E)-isomer. The height for which the concentrations in the air were calculated was 1.5 m, the same as the

Table 2: Input data for the PAL model used to calculate the dispersion of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in air after its injection into the soil of Field A.

| Interval after injection (days) | Rate of emission* ($\mu\text{g m}^{-2} \text{s}^{-1}$) | | Wind speed (m s^{-1}) | Wind direction (degrees) | Stability class (Pasquill) | Mixing height (m) |
|---------------------------------|--|--------|----------------------------------|--------------------------|----------------------------|-------------------|
| | (Z) | (E) | | | | |
| 1.1 | 0.05 | < 0.01 | 3.1 | 280 | D | 500 |
| 2.2 | 0.63 | 0.05 | 2.9 | 220 | D | 500 |
| 3.0 | 1.20 | 0.15 | 2.4 | 248 | D | 500 |
| 5.1 | 2.00 | 0.52 | 2.7 | 130 | D | 500 |
| 7.1 | 1.95 | 0.74 | 1.0 | 280 | B | 1 500 |
| 10.3 | 1.50 | 0.77 | 3.4 | 10 | D | 500 |

* (Z) = (Z)-1,3-dichloropropene

(E) = (E)-1,3-dichloropropene

In the PAL model the source strength is expressed as $\text{g m}^{-2} \text{s}^{-1}$.

Table 3: Input data for the PAL model used to calculate the dispersion of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in air after its injection into the soil of Field B.

| Interval after injection (days) | Rate of emission* ($\mu\text{g m}^{-2} \text{s}^{-1}$) | | Wind speed (m s^{-1}) | Wind direction (degrees) | Stability class (Pasquill) | Mixing height (m) |
|---------------------------------|--|--------|----------------------------------|--------------------------|----------------------------|-------------------|
| | (Z) | (E) | | | | |
| 1.0 | < 0.01 | < 0.01 | 2.8 | 160 | C | 1 000 |
| 1.8 | 0.01 | < 0.01 | 2.2 | 70 | D | 500 |
| 3.0 | 0.08 | < 0.01 | 3.7 | 60 | D | 500 |
| 3.8 | 0.17 | 0.01 | 5.0 | 160 | D | 500 |
| 6.1 | 0.43 | 0.05 | 5.9 | 140 | D | 500 |
| 9.1 | 0.68 | 0.14 | 6.5 | 185 | D | 500 |

* (Z) = (Z)-1,3-dichloropropene

(E) = (E)-1,3-dichloropropene

In the PAL model the source strength is expressed as $\text{g m}^{-2} \text{s}^{-1}$.

height at which the samples were taken in the field. A FORTRAN computer program, using graphical sub-routines,^{9,10} was made to present the results of each run in figures with concentration patterns. Concentration class boundaries were set at 0.2, 1.0, 5.0, 10.0 and $20 \mu\text{g m}^{-3}$.

2.3 Measurement of 1,3-dichloropropene in the air

The air was sampled with charcoal tubes (100 and 50 mg sections, SKC, petroleum-based) using portable sampling pumps, type Dupont P4000 or P4LC. Air samples were taken with two charcoal tubes in series. The second charcoal tube was used as a regular check on breakthrough of the fumigant from the first tube. Air samples

of 40 litres were taken at a rate of 40 litres h^{-1} . Van den Berg et al.¹¹ have shown that no breakthrough occurs when sampling air volumes up to 60 litres (at a rate of 60 litres h^{-1}).

At six time intervals in a period of up to ten days after the injection of the fumigant, air samples were taken around both fields in series at a height of 1.5 m above the soil surface. Each series consisted generally of two air samples taken upwind of the treated field (upwind distance between 25 and 50 m) and four or five air samples taken at sites downwind of the treated field. The charcoal tubes were stored in a cooling box at a temperature of a few degrees celsius or in a deep-freeze for up to about two days before they could be transported to the laboratory.

The charcoal samples were extracted on the day of their arrival at the laboratory. The contents of both sections of each charcoal tube were first combined and then extracted with 2 ml cooled acetone by shaking for one min. Sub-samples of 5 μl from the extracts were injected into a gas chromatograph (Perkin Elmer Sigma 2000) with a fused-silica capillary column (25 m long; 0.32 mm i.d.) coated with CP-Sil 5 CB (film thickness 1.2 μm ; Chrompack). The fumigant was measured by an electron-capture (EC) detector. The concentrations of fumigant in the extracts were calculated after measuring standard solutions of fumigant in acetone. More details on the analytical procedure have been presented by Van den Berg et al.¹¹ The desorption efficiency of acetone for a sample load corresponding to a concentration of 10 $\mu\text{g m}^{-3}$ of 1,3-dichloropropene in 40 litres of air, as determined by the phase equilibrium method, was 98% ($n=15$, s.d.=2.3%). The limit of detection of each isomer of 1,3-dichloropropene in air samples of 40 litres was 0.2 $\mu\text{g m}^{-3}$.

3 RESULTS AND DISCUSSION

3.1 Computations and measurements for Field A

The results of the computations for Field A are presented in figures with patterns of concentrations (height 1.5 m) of both isomers of 1,3-dichloropropene in air around the fumigated field for six time intervals after the injection of this fumigant into the soil. In these figures, the one-hour concentrations measured are rounded off to whole numbers and the measurement sites are indicated by triangles.

The patterns of concentrations of both isomers at an interval of 1.1 days after injection into the soil are presented in Figure 1-I. The concentrations calculated on the downwind edge of the treated field were at or below 0.6 and below 0.2 $\mu\text{g m}^{-3}$ for the (Z)-isomer and the (E)-isomer, respectively. The concentrations measured were higher: the concentrations of the (Z)-isomer and the (E)-isomer ranged up to 2.8 and 1.0 $\mu\text{g m}^{-3}$, respectively, at a downwind distance of approximately 100 m.

The patterns of concentrations of both isomers at an interval of 2.2 days after injection are presented in Figure 1-II. The computed concentrations were lower than those measured in the field. On the downwind edge of the field, the concentrations computed for the (Z)-isomer and the (E)-isomer were 4.6 and 0.4 $\mu\text{g m}^{-3}$, respectively, whereas those measured for the (Z)-isomer and the (E)-isomer were 11 and 2.8 $\mu\text{g m}^{-3}$. The concentrations measured for the (Z)-isomer and the (E)-isomer decreased to 3.4 and 0.8 $\mu\text{g m}^{-3}$, respectively, as the downwind distance increased to 175 m.

The patterns of concentration of both isomers at an interval of 3.0 days after injection are presented in Figure 1-III. The computed concentrations were still lower than those measured in the field. The computed concentrations of the (Z)-isomer and the (E)-isomer for the downwind edge of the field ranged up to 17 and 2.0 $\mu\text{g m}^{-3}$, respectively. The concentrations measured for the (Z)-isomer and the (E)-isomer decreased from 22 to 17 $\mu\text{g m}^{-3}$ and from 7.0 to 5.3 $\mu\text{g m}^{-3}$, respectively, as the downwind distance increased from 0 to about 100 m. A comparatively high concentration of the (Z)-isomer and of the (E)-isomer was measured upwind from the field: 5.0 and 2.7 $\mu\text{g m}^{-3}$, respectively. Because the average wind direction was almost parallel to the long edges of the field, a comparatively small change in the wind direction may have changed the status of the measurement site from 'upwind' to 'downwind'.

The patterns of concentration of both isomers at an interval of 5.1 days after injection are presented in Figure 2-I. The concentrations computed for the (Z)-isomer were somewhat higher than those measured, but there was no clear difference for the (E)-isomer. The computed concentrations of the (Z)-isomer and the (E)-isomer for the downwind edge ranged up to 17 and 4 $\mu\text{g m}^{-3}$, respectively. The concentrations of the (Z)-isomer measured decreased from 10 to 1.1 when increasing the distance from the field from 0 to about 200 m. The corresponding decrease in the concentration measured for the (E)-isomer was from 5.7 to 0.5 $\mu\text{g m}^{-3}$.

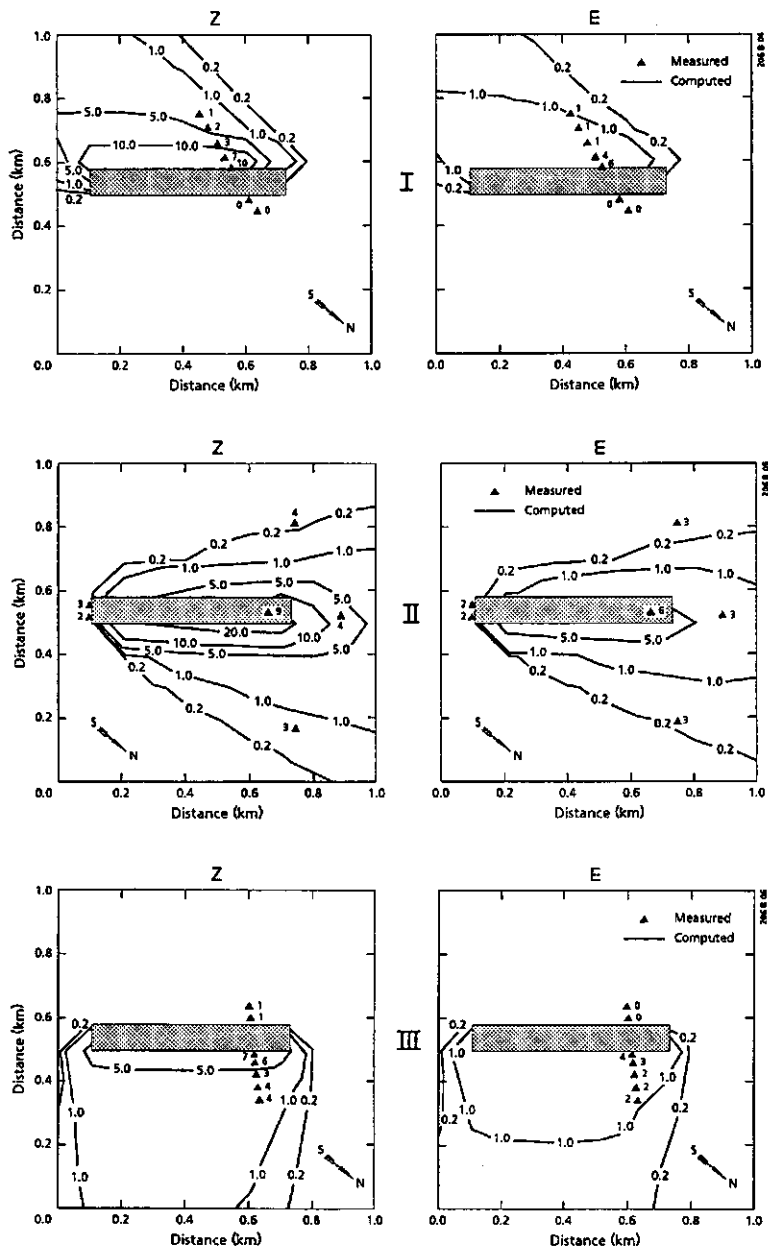


Fig. 2: Concentration patterns of (Z)-1,3-dichloropropene (Z) and (E)-1,3-dichloropropene (E) in the air computed for Field A at 5.1 (I), 7.1 (II), and 10.3 (III) days after injection of the fumigant into the soil. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

The patterns of concentration of both isomers at an interval of 7.1 days after injection are presented in Figure 2-II. The order of magnitude was the same for the computed concentrations and those measured. The concentrations of the (Z)-isomer and the (E)-isomer computed at the downwind edge ranged up to about 26 and 10 $\mu\text{g m}^{-3}$, respectively. During sampling, the wind speed was low (1.0 m s^{-1}) and the wind direction variable. In the computations it had to be assumed that the wind direction remained the same during one-hour periods. Because of the variable wind direction, no real upwind sites could be distinguished in the measurements.

The patterns of concentration of both isomers at an interval of 10.3 days after injection are presented in Figure 2-III. At this time, the concentrations computed corresponded roughly to those measured in the field. The concentration measured for the (Z)-isomer decreased from 7.0 to 3.6 $\mu\text{g m}^{-3}$ at a downwind distance increasing from about 20 to 170 m; those measured for the (E)-isomer were somewhat lower: they decreased from 4.1 to 2.1 $\mu\text{g m}^{-3}$. A distinct concentration of 1,3-dichloropropene was measured at an upwind distance of 30 m: 1.2 $\mu\text{g m}^{-3}$. This may have been caused by the treatment of a field upwind from the measuring site. However, no detailed observations of fumigation practices upwind of Field A were made at that time.

For the most relevant sampling series, the concentrations of both isomers in air computed for the sites where air samples were taken and those measured are summarized in Table 4. At 2.2 and 3.0 days after injection, the computed concentrations were distinctly lower than those measured. However, at 5.1 and 10.3 days after injection, the computed and measured concentrations were of the same order of magnitude.

During the first three days following injection into the soil, the ratio between the (Z)-isomer and the (E)-isomer for the measurements at sites downwind from the field ranged from 2.7 to 5.3. The ratio between the concentrations of the (Z)-isomer and the (E)-isomer in Telone II is approximately 1.2. The higher ratio for the measurements in air can be explained by the higher volatility of the (Z)-isomer as compared to that of the (E)-isomer. During the period from five to ten days after injection, the ratio ranged from 1.2 to 2.2. Because the ratio between the amounts of the (Z)-isomer and the (E)-isomer remaining in soil decreases in the course of time, a corresponding decrease can be expected for the ratio between the rates of the emission of the (Z)-isomer and (E)-isomer. The ratio between the computed rates of emission of the (Z)-isomer and the (E)-isomer from soil (Table 2) decreased from 13 at 2 days after injection to 1.9 at 10 days. It should be noted that during the first ten days after injection, the computed concentrations of the (Z)-isomer in air were higher than those for the (E)-isomer and that the same difference was found in the measurements.

Table 4: Computed and measured concentrations of (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene in the air downwind of Field A after its injection.

| Time after injection (d) | Downwind distance (m) | Concentration in air ^a ($\mu\text{g m}^{-3}$) | | | |
|-----------------------------|--------------------------|--|-----|----------|-----|
| | | computed | | measured | |
| | | Z | E | Z | E |
| 2.2 | 0 | 4.6 | 0.4 | 11 | 2.8 |
| 2.2 | 73 | 2.7 | 0.2 | 7.3 | 1.8 |
| 2.2 | 105 | 2.2 | 0.2 | 5.5 | 1.4 |
| 2.2 | 175 | 1.7 | 0.1 | 3.4 | 0.8 |
| 3.0 | 0 | 17 | 2.0 | 22 | 7.0 |
| 3.0 | 104 | 7.6 | 0.9 | 17 | 5.3 |
| 5.1 | 0 | 17 | 4.4 | 10 | 5.7 |
| 5.1 | 39 | 11 | 2.9 | 7.4 | 4.3 |
| 5.1 | 88 | 7.3 | 1.9 | 2.8 | 1.4 |
| 5.1 | 135 | 5.1 | 1.3 | 2.0 | 1.0 |
| 5.1 | 204 | 3.3 | 0.8 | 1.1 | 0.5 |
| 10.3 | 20 | 7.3 | 3.9 | 7.0 | 4.1 |
| 10.3 | 54 | 5.2 | 2.8 | 5.6 | 3.1 |
| 10.3 | 92 | 4.0 | 2.1 | 3.0 | 1.7 |
| 10.3 | 130 | 3.3 | 1.7 | 3.7 | 2.3 |
| 10.3 | 173 | 2.7 | 1.4 | 3.6 | 2.1 |

^a (Z) = (Z)-1,3-dichloropropene

(E) = (E)-1,3-dichloropropene

3.2 Computations and measurements for Field B

The computed and measured one-hour concentrations of both isomers of 1,3-dichloropropene in air around Field B are presented in the same way as those for Field A.

The patterns of concentrations of both isomers at a height of 1.5 m at an interval of 1.0 day after injection are presented in Figure 3-I. The concentrations in the air computed for both (Z)-1,3-dichloropropene and (E)-1,3-dichloropropene were below $0.2 \mu\text{g m}^{-3}$. The concentrations measured for the (Z)-isomer were higher: they decreased from 1.2 to $0.4 \mu\text{g m}^{-3}$ when increasing the downwind distance from 0 m to 260 m. The concentration measured for the (E)-isomer just reached the detection limit of $0.2 \mu\text{g m}^{-3}$ at distances downwind from the field ranging from 0 to 180 m, but it was below $0.2 \mu\text{g m}^{-3}$ at a downwind distance of 260 m.

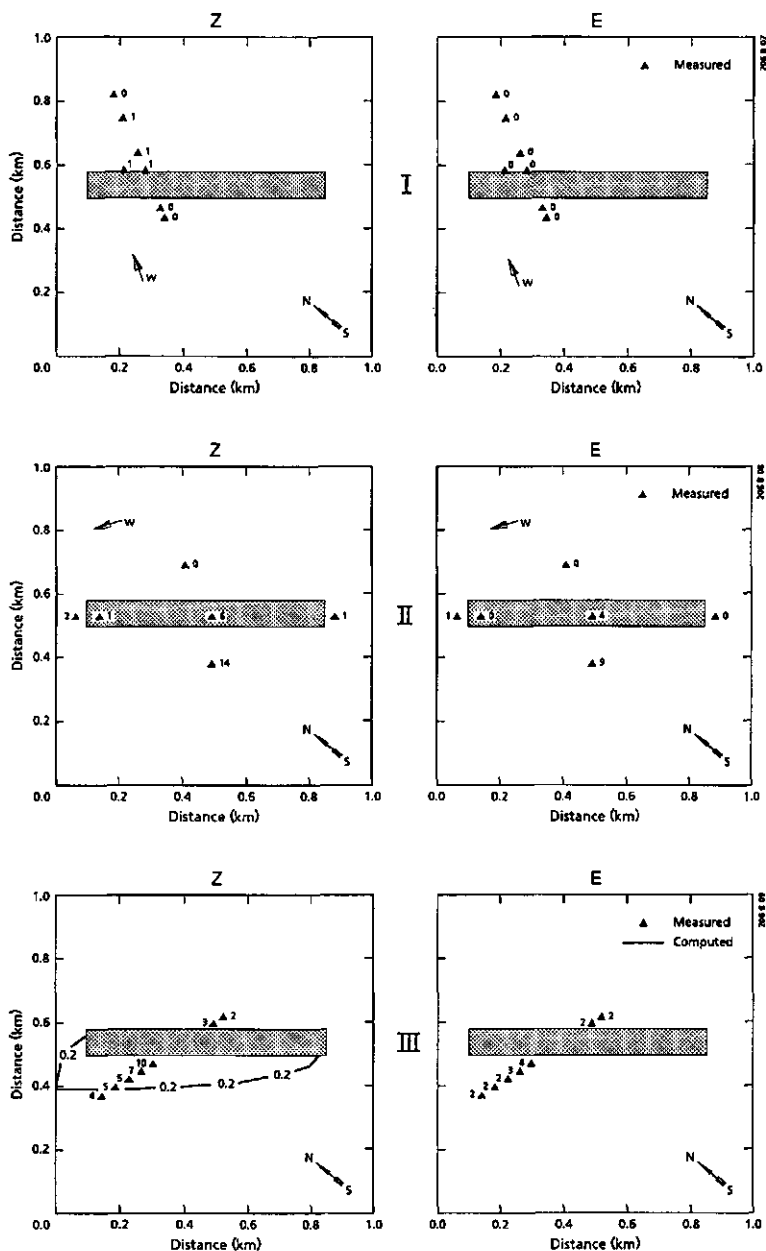


Fig. 3: Concentration patterns of (Z)-1,3-dichloropropene (Z) and (E)-1,3-dichloropropene (E) in the air computed for Field B at 1.0 (I), 1.8 (II), and 3.0 (III) days after injection of the fumigant into the soil. No iso-concentration lines are given if computed concentrations are below $0.2 \mu\text{g m}^{-3}$. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated. Arrow with w = wind direction.

The patterns of concentration of both isomers at an interval of 1.8 days after injection are presented in Figure 3-II. The concentrations computed were lower than those measured: they remained below $0.2 \mu\text{g m}^{-3}$ for both isomers. During this sampling period (from 8.45 until 9.45 h Central European Time) wind speed was comparatively low, i.e. 2.2 m s^{-1} and the variation in the wind direction was comparatively high: about 70° . The concentrations measured for the (Z)-isomer and the (E)-isomer at a distance of about 100 m from the downwind edge of the field were 14 and $9.4 \mu\text{g m}^{-3}$, respectively.

The patterns of concentrations of both isomers at an interval of 3.0 days after injection are presented in Figure 3-III. Again, the concentrations computed for the downwind edge of the field were lower than those measured: the concentration computed for the (Z)-isomer was about $0.6 \mu\text{g m}^{-3}$ and that for the (E)-isomer was below $0.2 \mu\text{g m}^{-3}$. The concentrations measured for the (Z)-isomer ranged from $9.6 \mu\text{g m}^{-3}$ at a distance of 30 m downwind of the field to $4.3 \mu\text{g m}^{-3}$ at a distance of 210 m. The corresponding range for the (E)-isomer was from 3.6 to $1.7 \mu\text{g m}^{-3}$. Distinct concentrations of the (Z)-isomer and of the (E)-isomer were measured at a site at about 50 m upwind from a position of half-way along the long edge of the treated field: 2.4 and $1.6 \mu\text{g m}^{-3}$, respectively. This upwind site may have been influenced by a neighbouring field SE of Field B, which was injected with 1,3-dichloropropene on the afternoon of the second day after the day Field B had been injected. The size of the neighbouring field is similar to that of Field B and its long edges are parallel to those of Field B.

The patterns of concentrations of both isomers at an interval of 3.8 days after injection are presented in Figure 4-I. The computed downwind concentrations corresponded roughly to those measured in the air: on the downwind edge they ranged up to about 1.0 and $0.1 \mu\text{g m}^{-3}$, for the (Z)-isomer and the (E)-isomer, respectively. The concentrations measured for the (Z)-isomer decreased from 0.8 to $0.5 \mu\text{g m}^{-3}$ when the downwind distance increased from 35 to 250 m. The concentration of the (Z)-isomer measured on the downwind edge was below $0.2 \mu\text{g m}^{-3}$, for which no explanation can be given. One hour later, the concentrations of the (Z)-isomer measured at the same sites were similar, except that this time the concentration of this isomer at the downwind edge was $1.1 \mu\text{g m}^{-3}$. The concentration of the (E)-isomer was $0.2 \mu\text{g m}^{-3}$ up to distances of 80 m downwind of the field, and further downwind it was below $0.2 \mu\text{g m}^{-3}$.

The patterns of concentrations of both isomers at an interval of 6.1 days after injection are presented in Figure 4-II. The concentrations computed for the (Z)-isomer were slightly higher than those measured in the field: on the downwind edge the computed concentrations ranged up to about $1.6 \mu\text{g m}^{-3}$ and those measured ranged up to about $0.7 \mu\text{g m}^{-3}$. Both the concentrations measured and those computed for the (E)-isomer ranged up to about $0.2 \mu\text{g m}^{-3}$. At a distance of 80 m downwind of the field, the concentration measured for the (Z)-isomer was $0.4 \mu\text{g m}^{-3}$, while that for the (E)-isomer fell below the detection limit.

The patterns of concentration of both isomers at an interval of 9.1 days after injection are presented in Figure 4-III. The concentrations computed for the (Z)-isomer in air

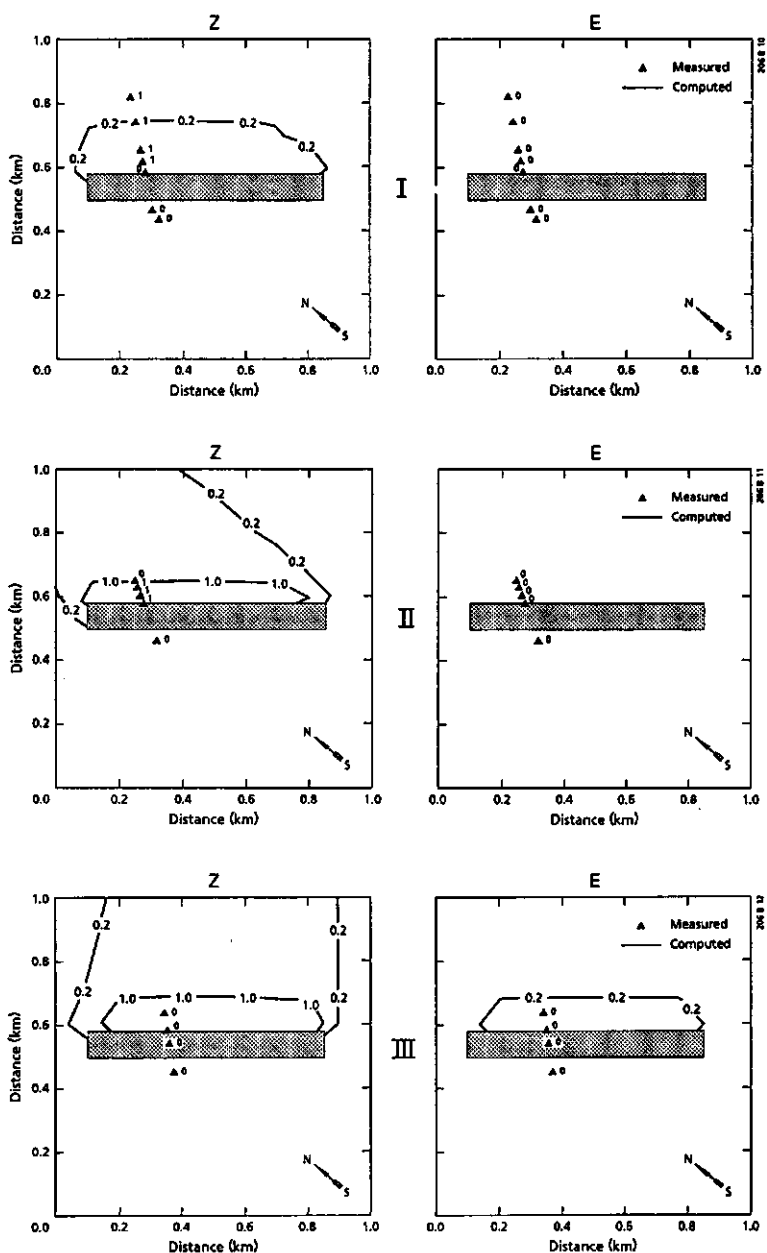


Fig. 4: Concentration patterns of (Z)-1,3-dichloropropene (Z) and (E)-1,3-dichloropropene (E) in the air computed for Field B at 3.8 (I), 6.1 (II), and 9.1 (III) days after injection of the fumigant into the soil. No iso-concentration lines are given if computed concentrations are below $0.2 \mu\text{g m}^{-3}$. Concentrations measured ($\mu\text{g m}^{-3}$) also indicated.

were somewhat higher than those measured in the field, but the concentrations computed for the (E)-isomer roughly corresponded with those measured. The concentrations of the (Z)-isomer and the (E)-isomer in air computed for the downwind edge ranged up to about 1.9 and 0.4 $\mu\text{g m}^{-3}$, respectively. The concentrations of the (Z)-isomer measured on the downwind edge and at a downwind distance of about 50 m were about 0.4 $\mu\text{g m}^{-3}$ and those measured for the (E)-isomer at those sites just reached 0.2 $\mu\text{g m}^{-3}$.

During the first three days following the injection of 1,3-dichloropropene into the soil, the ratio between the concentrations of the (Z)-isomer and the (E)-isomer as measured at sites downwind from the field was higher than that for the product: it ranged from 1.5 to 6.0. During the period from four to nine days after injection, the ratio ranged from 2.0 to 5.5. However, during that period about half of the downwind concentrations measured for the (E)-isomer in air just reached the detection limit and only for this fraction of samples could the ratio be calculated.

4 GENERAL DISCUSSION AND CONCLUSIONS

During the first three days after injection of 1,3-dichloropropene into the soil of Field A, the one-hour concentrations in air measured were higher than those computed. This indicates that the rate of emission from this field increased more rapidly than was derived from the computations by Van den Berg and Leistra.⁵ The unexpectedly high rate of diffusion of fumigant to the soil surface may have been caused by heterogeneities in soil structure, resulting from pulling the injector blades through the soil and from remnants of the previous crop, or by a locally shallower depth of injection. Such complications were not accounted for in the computer-simulation model used to calculate the rate of emission of fumigant into the air. Measurement of the contents of both isomers of 1,3-dichloropropene in soil, albeit on a limited scale, also indicated that the upward movement of fumigant in the soil of this field was faster than that computed.⁵ For the period from five to ten days after injection, in general, the computed and measured concentrations of the isomers in air were at the same level.

During the first three days after injection of 1,3-dichloropropene into the soil of Field B, the one-hour concentrations in air measured were higher than those computed. Again, this indicates a faster upward movement of fumigant to the soil surface after injection than was computed by Van den Berg and Leistra.⁵ However, a limited number of measurements on the contents of both isomers in the soil of this field did not indicate more rapid upward diffusion than computed. For the period from four to nine days after injection, the computed concentrations of the isomers in air roughly corresponded to those measured.

The lower concentrations in the air computed for Field B on the days following application, compared with those for Field A, can be explained by the lower volume fractions of the gas phase in the 0.0 - 0.2 m layer, resulting in a lower rate of emission into the air.⁵ This lower rate of emission for Field B is confirmed by the generally lower concentrations measured in air around Field B as compared to those measured around Field A.

The higher concentrations measured in air during the first period after injection, compared with those computed, indicate that the actual extent of emission of 1,3-dichloropropene into the air was higher than that computed by Van den Berg and Leistra.⁵ Continued attention is needed for the structural condition of the soil as well as for the finishing-off of the soil surface to prevent unexpectedly high rates of emission via larger voids in the soil.

The concentrations of 1,3-dichloropropene in air measured around both fields on the days following the day of injection ranged up to $29 \mu\text{g m}^{-3}$. However, Van den Berg et al.¹¹ measured comparatively high one-hour concentrations in air during the injection of this fumigant into the soil: up to $506 \mu\text{g m}^{-3}$ on the downwind edges of the field (height 1.5 m). Presumably, these concentrations result from fumigant dripping from the nozzles on the soil surface when the blades are lifted out of the

soil at the end of the fumigation strips. Information is available on short-term effects of concentrations in air exceeding $5\,000\ \mu\text{g m}^{-3}$, i.e. the maximum acceptable concentration in air for occupational exposure, but little research is published on effects of chronic exposure to concentrations below this level.¹² Therefore, it may be necessary to minimize exposure to concentrations in air by improvement of the application technique.

Albrecht and Chenchin¹³ measured concentrations of 1,3-dichloropropene in air at a height of 1.0 m above a treated row (dosage of $293\ \text{l ha}^{-1}$), which was covered with $25\ \mu\text{m}$ thick poly-ethene film after injection of the fumigant at a depth of 0.45 m. During the measuring period, the soil temperature at injection depth was $26\ ^\circ\text{C}$ and the average moisture content of the soil at injection depth was 30%. The concentration of 1,3-dichloropropene increased to about $3\,000\ \mu\text{g m}^{-3}$ at 1.0 d after injection. During the next day, the concentration in air dropped sharply to about $70\ \mu\text{g m}^{-3}$, but thereafter the decrease was more gradual until a concentration of about $0.7\ \mu\text{g m}^{-3}$ was reached at 20 d after injection. In our study, the concentrations of 1,3-dichloropropene in air measured after injection into the soil at 0.15 to 0.20 m were much lower. Presumably, the rate of emission in the study of Albrecht and Chenchin¹³ reached higher levels because of the higher soil temperature: $26\ ^\circ\text{C}$ versus 6 to $9\ ^\circ\text{C}$ for the fields in our study.

Albrecht and Chenchin¹³ measured an almost tenfold increase in the concentration of 1,3-dichloropropene in air (height 1.0 m) at 6 d after injection into the soil, following 6 mm of rainfall during the preceding evening. In our study, several mm of rainfall were recorded for field B on day 5. However, after this rainfall no clear increase in the concentration in air was measured. This may have been caused by the moist condition of the top layer of Field B: shortly after injection the moisture content in the upper 0.05 m layer was 42% and evaporation thereafter was low.⁵ Pesticides are adsorbed more strongly by soils at very low moisture contents (below a few percent, depending on texture and organic matter content) resulting in comparatively low volatilization losses.¹⁴ The moisture content of the surface soil layer of the field studied by Albrecht and Chenchin¹³ may have been below this level before the rainfall on day 6.

Due to the uncertainties in the source strength of the emission of fumigant into the air as introduced in the PAL model, the tracing of possible shortcomings in the model for vapour dispersion in air is not possible. Values for the Pasquill stability class were taken from the nearest weather station, located at a distance of about 35 km from the fumigated fields. The actual stability condition of the air around the fumigated fields may have been different from that at the weather station, for example as a result of differences in the rate of breakdown of a night-time inversion layer. A different Pasquill stability class affects the concentrations computed with a gaussian plume model substantially, because different values for the dispersion coefficients have to be used.^{15,16} The stability condition of the atmosphere at the measurement site may be checked by measuring wind speed at a single height and air temperature at two heights, e.g. at 2 and 10 m.¹⁷

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**7 CONCENTRATIONS OF 1,3-DICHLOROPROPENE AND METHYL
ISOTHIOCYANATE IN AIR IN A REGION WITH INTENSIVE USE OF
SOIL FUMIGANTS**

Submitted for publication

CONCENTRATIONS OF 1,3-DICHLOROPROPENE AND METHYL
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ABSTRACT

A sampling programme was set up to measure 1,3-dichloropropene and methyl isothiocyanate in air in a region with intensive agricultural use of these soil fumigants. In two consecutive autumns, 6-hour air samples were taken at two locations in that region with charcoal tubes using automatic samplers. Most (81%) of the 6-hour concentrations of 1,3-dichloropropene measured in both years were below $3.2 \mu\text{g m}^{-3}$ and a few percent could not be measured with a detection limit of around $0.3 \mu\text{g m}^{-3}$. Only 4% of the 6-hour concentrations exceeded $10 \mu\text{g m}^{-3}$, almost all of which were measured at a location where a field just upwind of the measuring site had been treated. For methyl isothiocyanate, 73% of the 6-hour concentrations of both years could not be measured with a detection limit in the two years of 1 and $2 \mu\text{g m}^{-3}$, respectively. A small fraction (3%) of the concentrations were in the range of 3.2 to $10 \mu\text{g m}^{-3}$ and only 1% exceeded $10 \mu\text{g m}^{-3}$.

The rates of emission of 1,3-dichloropropene and methyl isothiocyanate into air were estimated for weeks with many applications in the region studied. Using the PAL model, the concentration of fumigant in air at a receptor site was computed for representative fumigations at different upwind positions. The computed concentrations in air ranged up to $9.9 \mu\text{g m}^{-3}$ for 1,3-dichloropropene and up to $2.5 \mu\text{g m}^{-3}$ for methyl isothiocyanate.

1 INTRODUCTION

Arable soils are regularly fumigated in the cultivation of potatoes to prevent the development of large populations of soil-borne pathogens. Such populations would otherwise build up as a result of intensive farming practices. The soil fumigants frequently applied are 1,3-dichloropropene and metham-sodium. Although the latter chemical is not volatile, in the soil it is quickly transformed (largely within a day) into the volatile compound, methyl isothiocyanate. Following injection into the soil at a depth of 0.15 to 0.20 m, a fraction of the volatile compounds diffuses up to the soil surface and escapes into the air.

The arable region in the northeast of the Netherlands, the Veenkoloniën, consists of an area of about 1 200 km². In this region, many fields are fumigated in the autumn with 1,3-dichloropropene or metham-sodium. Until recently, it was mandatory to report the fumigations to the Plant Protection Service in order to obtain permission to cultivate potatoes every two years. Soil treatments between November 15 and March 15 are not permitted. The use of metham-sodium tends to be evenly spread throughout the period from September to November. More 1,3-dichloropropene is used as the weather gets colder because it is considered to be more effective than metham-sodium at low soil temperatures. When the topsoil dries out, fewer fields tend to be fumigated.

Application of fumigants does not solely result in exposure of contractors but may also lead to a certain degree of exposure of people living nearby. In the Netherlands, the maximum acceptable concentration of 1,3-dichloropropene in air, as a time-weighted average for exposures of up to 8 h per day with a maximum of 40 h per week, amounts to 5 mg m⁻³.¹ This concentration is equal to the Threshold Limit Value (time-weighted average) as adopted by the American Conference of Governmental Hygienists.² For methyl isothiocyanate, no maximum acceptable concentration has yet been adopted.¹ Questions arose on the concentrations of 1,3-dichloropropene and methyl isothiocyanate in the air after their application. Because little was known about the concentrations of fumigants in air, an air sampling programme was set up. In the autumn of two consecutive years, 6-hour air samples were taken regularly at two locations in the Veenkoloniën. Using a dispersion model for gaseous compounds in air, the influence of the distance between the measuring point and an upwind fumigated field was evaluated for different atmospheric conditions. Further, during weeks when many applications were done, the concentration of each of the fumigants in air at a receptor site was calculated for situations with representative fumigations at different upwind distances, under meteorological conditions approaching those of the weeks simulated. The calculated concentrations of each of the fumigants in air are compared with those measured in the same periods.

2 MATERIALS AND METHODS

2.1 Measurement of the fumigants in the air

In the autumns of 1986 and 1987, automatic samplers were placed at two locations in the Veenkoloniën: one in Valthermond (Drenthe Province) and the other in Borgercompagnie (Groningen Province). The village of Valthermond, built alongside a road oriented SW-NE, is surrounded by arable land extending several kilometres. The village of Borgercompagnie, also built alongside a road, is oriented NNW-SSE. Apart from the city of Veendam, situated about one kilometre to the east, the land stretching for several kilometres to the north, west and south is used as arable land.

The automatic samplers ("merry-go-rounds", type Euroglas) were installed in housings placed in the field at a distance of 0.2 to 0.25 km from the farmhouse. The samplers required a mains voltage of 220 V. The air was drawn through teflon tubing from the sampling height of 1.5 m into a glass bulb of the sampler with twelve sampling channels. Two sampling tubes in series were connected to each of these channels. The sampling tubes used to collect the fumigants in air contained charcoal (petroleum-based, 100/50 mg, SKC) as adsorbent. The second tube was used as a check on breakthrough of the fumigant from the first charcoal tube. At 6 hourly intervals, the sampler shifted to a following sampling channel. Special glass capillaries were used to regulate the flow of air to the automatic samplers. A capillary orifice was selected to sample at a rate of 6 L h^{-1} . In a study on the retention of 1,3-dichloropropene and methyl isothiocyanate on charcoal, van den Berg *et al.*³ showed that no breakthrough of fumigant from the first charcoal tube occurs when taking 40 litre samples (at a rate of 7 L h^{-1}). The charcoal tubes were removed from the sampling apparatus and replaced by new ones at intervals of up to about two days. The charcoal tubes were stored in a cooling box at a few degrees celsius (for the 1986 samples) or in a refrigerator freezer (for the 1987 samples) for up to about one day before they could be transported to the laboratory, where they were kept in a freezer until analysis.

The contents of both sections of each charcoal tube were first combined and then extracted with 2 ml cooled acetone. A subsample of $5 \mu\text{l}$ was injected into a gas chromatograph (Perkin Elmer Sigma 2000) with a fused-silica capillary column (25 m long; 0.32 mm i.d.) coated with CP-Sil 5 CB (film thickness $1.2 \mu\text{m}$; Chrompack). 1,3-Dichloropropene was determined by an electron capture detector and methyl isothiocyanate by a nitrogen-phosphorus detector. The concentrations of the fumigant in the extracts were calculated after measuring standard solutions of fumigant in acetone. For the 1986 measurements, the limits of detection of 1,3-dichloropropene and methyl isothiocyanate, when sampling 40 L of air, were 0.4 and $2.0 \mu\text{g m}^{-3}$, respectively. For the 1987 measurements somewhat lower detection limits were reached: 0.2 and $1 \mu\text{g m}^{-3}$, respectively. More details on the analytical procedure have been presented by van den Berg *et al.*³.

In the autumn of 1986, most of the samples of 1,3-dichloropropene in air were taken in November. In the autumn of 1987, samples were taken throughout the fumigation period from mid-September until mid-November. Methyl isothiocyanate in the air was sampled throughout the latter period in both years. Data on the area treated weekly with each of these fumigants in the autumn of 1987 were obtained from the Plant Protection Service and are presented in Table I. Most of the 1,3-dichloropropene was applied in the first half of November. The use of metham-sodium was more evenly spread throughout the period from mid-September until mid-November. During the measuring period, the fields treated with the fumigants in the neighbourhood of the automatic samplers were recorded, because not all fumigations were reported to the Plant Protection Service.

Information on wind speed and wind direction relevant to the sampling at the two locations was obtained from the weather station of the KNMI at Eelde airport (Drenthe Province).^{4,5} Information on atmospheric stability was also obtained from this weather station. The stability of the atmosphere at the sampling locations was assumed to be the same as that at the meteorological station at Eelde airport. The measuring points at Borgercompagnie and Valthermond were about 20 and 35 km, respectively, from the airport.

Table I. Area treated with 1,3-dichloropropene or metham-sodium in the northeast of the Netherlands in autumn 1987 (Plant Protection Service, 1988).

| Month | Week number | Area treated (ha) | |
|-----------|-------------|---------------------|---------------|
| | | 1,3-dichloropropene | metham-sodium |
| September | 37 | 9 | 243 |
| | 38 | 14 | 959 |
| | 39 | 50 | 1 399 |
| | 40 | 55 | 1 566 |
| October | 41 | 87 | 1 005 |
| | 42 | 46 | 568 |
| | 43 | 54 | 1 135 |
| | 44 | 220 | 1 271 |
| November | 45 | 585 | 1 895 |
| | 46 | 834 | 1 318 |

2.2 Computation of the concentrations in air

To compute concentrations of fumigant in air above and around treated fields, information is needed on the amounts of fumigant emitted to the atmosphere after its injection into the soil. Such information can be obtained using a computer-simulation model for fumigant behaviour in soil. The elements for such a model have been described by Siebering and Leistra⁶. The spread through the soil of 1,3-dichloropropene and methyl isothiocyanate occurs predominantly by diffusion through the gas-filled pore system due to the volatility of the compounds. The transformation of the fumigant in soil is usually described by first-order kinetics. Computations on the emission of the fumigant into the air after injection into the soil using such a model have shown that most of the emission takes place in the first three weeks following application.⁷ For the first, second and third weeks following application of 1,3-dichloropropene (end October 1987), the percentages of (Z)-isomer calculated to be lost by volatilization from a soil representative for the northeast of the Netherlands were 8%, 10% and 4% of the dosage, respectively. For the (E)-isomer, these percentages were 2%, 6% and 4%, respectively. During the first three weeks following application of metham-sodium (end September 1987), the amounts of methyl isothiocyanate calculated to be lost by volatilization from a representative soil were 4%, 5% and 2% of its equivalent dosage, respectively.⁷

The dispersion of gases and vapours in air following emission from area sources in level terrain can be calculated using the PAL model.⁸ This is a model developed by the U.S. Environmental Protection Agency and is based on the Gaussian plume concept. Despite its limitations, this concept is generally used to compute the short-range dispersion of air pollutants from area sources.⁹ In our study, a modified set of dispersion coefficients recommended for use for ground-level sources by the TNO Working Group "Dispersion Air Pollutants"^{10,11} was introduced. The values recommended for the vertical dispersion coefficients also depend on the roughness length. The roughness length for the present calculations was taken as 0.05 m, which is assumed to correspond to the roughness of the surface in the region studied.

The necessary input data for each area source (square or rectangle), consist of its size (km), position and orientation, its height (m) and its strength ($\text{g m}^{-2} \text{s}^{-1}$). Meteorological data used by the PAL model include wind speed (m s^{-1}), wind direction (degrees), atmospheric stability (Pasquill stability class) and mixing height (m). The height of the air layer in which mixing takes place depends on the atmospheric stability and the heights corresponding to each of the Pasquill stability classes were set at the values recommended by the TNO Working Group "Dispersion Air Pollutants".¹¹ The mixing height under neutral conditions, Pasquill stability type D, is taken as 0.5 km. Under stable atmospheric conditions the mixing height is less than 0.5 km and under unstable conditions the value is greater.

First, this PAL model was used to assess the influence of the distance between the fumigated field and measuring point (receptor) on the concentration at the receptor under different atmospheric stability conditions. An area of 10.0 (W-E) by 10.5 km (N-S) was divided into squares of 0.5 by 0.5 km. Each square had an area source of 0.5 by 0.1 km situated next to its eastern border with the longer sides of the area

source perpendicular to the wind direction, i.e. 270° (grid-north is at 0°). The receptor was located midway on the downwind edge (N-S) of the simulated area at a height of 1.5 m above the ground. The strength of each area source was taken to be $1.0 \cdot 10^{-6} \text{ g m}^{-2} \text{ s}^{-1}$, which is in the range of emission maxima of the isomers of 1,3-dichloropropene and methyl isothiocyanate reported by Van den Berg and Leistra⁷. The wind speed was set at 4.0 m s^{-1} , being the average wind speed measured at Eelde airport during October and November 1987. Computations were done for three stability conditions, type A (very unstable), type D (neutral) and type F (stable).

Computations were made to assess the ambient concentration of the fumigants during the period when many applications were carried out. Week 45 (early November) was simulated for 1,3-dichloropropene and for methyl isothiocyanate the more representative week 41 (early October, see Table I). For these simulations, fumigations in the two preceding weeks also need to be taken into account. Data on the area treated with 1,3-dichloropropene during weeks 43, 44 and 45 and on the area treated with metham-sodium during weeks 39, 40 and 41 were obtained from the Plant Protection Service (see Table I).

An area of 7.5 by 1.5 km was considered with the longer sides oriented W-E, and divided into squares of 0.5 by 0.5 km. The receptor was located midway on the eastern edge of this area. The wind direction for the whole calculation series was taken as 270° (grid north at 0°). The simulated area is represented in Figure 1. Under neutral atmospheric conditions (Pasquill type D), reported frequently to occur at Eelde airport in the autumn, it was calculated that fumigations outside this area contribute hardly to the concentration at the receptor. Within the simulated area there were three fields, each 0.500 by 0.055 km in size and with the longer sides perpendicular to the wind direction, corresponding to the area of the Veenkoloniën treated with 1,3-dichloropropene in weeks 43, 44 and 45. These three fields (See Figure 1) were divided over the three rows. The source strength was assumed to be the same for each area source.

The dosage of 1,3-dichloropropene used for nematode control in potatoes is 150 litres per hectare. One of the commercial products, Telone II, contains 1.1 kg 1,3-dichloropropene per litre and the ratio of the (Z)-isomer to the (E)-isomer in this

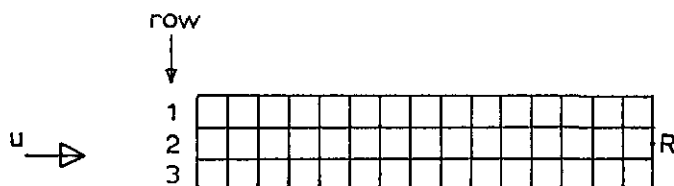


Fig. 1 Lay out of the area used for the simulation of the effect of fumigations on the concentration at receptor point R. Size area: 7.5 by 1.5 km. Arrow with u =wind direction.

product is 1.2. Therefore, 89.7 kg of the (Z)-isomer and 76.5 kg of the (E)-isomer of 1,3-dichloropropene are applied per hectare. The amount of 1,3-dichloropropene lost by volatilization during a week was calculated from the percentages of the dosage computed to be lost for the fumigations in that week and for those of the two preceding weeks. For the (Z)-isomer, it was calculated that the loss by volatilization in week 45 was 7%, 9% and 4% of the amounts applied in weeks 43, 44 and 45, respectively. For the (E)-isomer the percentages were 5%, 4% and 1%, respectively. For a total area of 859 ha treated in the Veenkoloniën during weeks 43, 44 and 45 (see Table I), the amount of (Z)-isomer calculated to be emitted into the atmosphere in week 45 was approximately 4 200 kg and that for the (E)-isomer approximately 1 300 kg. For this area, the average rates of emission during week 45 amounted to $8.1 \cdot 10^{-7}$ and $2.6 \cdot 10^{-7} \text{ g m}^{-2} \text{ s}^{-1}$, for the (Z)- and the (E)-isomer, respectively, resulting in a total rate of emission of $1.07 \cdot 10^{-6} \text{ g m}^{-2} \text{ s}^{-1}$.

For 80% of the hourly periods of week 45, atmospheric stability conditions were neutral, Pasquill stability class D,⁵ and this was assumed to be representative for week 45. The average wind speed in week 45 was 2.1 m s^{-1} at 10 m .⁵ For neutral atmospheric conditions, the logarithmic wind profile formula can be used to calculate the average wind speed at sampling height, i.e. 1.5 m .¹² This resulted in a wind speed of 1.4 m s^{-1} and this value was used in the calculations. Several simulations were done with fumigated fields at different distances from the receptor.

Computations similar to that for 1,3-dichloropropene were set up for methyl isothiocyanate. Within the simulated area there were nine fields, each 0.500 by 0.085 km in size and with the longer sides perpendicular to the wind direction, corresponding to the area of the Veenkoloniën treated with metham-sodium in weeks 39, 40 and 41. These nine fields (See Figure 1) were divided over the three rows. Further, the fields within each W-E row were regularly distributed: one field per 2.5 km interval in upwind direction from the receptor.

The dosage of metham-sodium for nematode control in potatoes is 153 kg per hectare (applied as an 0.51 kg l^{-1} aqueous solution). The percentages of the equivalent amounts of methyl isothiocyanate applied during weeks 39, 40 and 41, corresponding to those of its precursor metham-sodium, computed to be emitted into the atmosphere in week 41 were 3.5%, 4.5% and 2.0%, respectively. For a total area of $3\,970 \text{ ha}$ treated in the Veenkoloniën during weeks 39, 40 and 41, the amount of methyl isothiocyanate calculated to be emitted into the atmosphere in week 41 was therefore approximately $12\,100 \text{ kg}$. Consequently, the average rate of emission of methyl isothiocyanate amounted to $5.0 \cdot 10^{-7} \text{ g m}^{-2} \text{ s}^{-1}$.

For about 80% of the hourly periods in week 41, the atmospheric stability conditions were neutral, Pasquill stability class D,⁵ and this was assumed to be representative for week 41. The average wind speed in week 41 was 5.9 m s^{-1} at 10 m .⁵ The logarithmic wind profile formula was used to calculate the wind speed at sampling height.¹² This resulted in a wind speed of 3.8 m s^{-1} and this value was used in the calculations. In the computations, although the position of the field in the central row closest to the receptor was changed to other positions in the same row, the positions of the other eight fumigated fields remained unchanged.

3 RESULTS

3.1 Measurements of 1,3-dichloropropene

The 6-hour concentrations of 1,3-dichloropropene [(Z)- plus (E)-isomer] measured in the autumn of 1986 at the two sampling locations are shown in Figure 2. The fractions of concentrations within several classes also given in this Figure. The percentages of the 6-hour concentrations measured at the Valthermond and the Borgercompagnie locations that remained below $3.2 \mu\text{g m}^{-3}$ were 81% ($n=39$) and 72% ($n=33$), respectively. At the Valthermond location, 8% ($n=4$) of the concentrations was below the detection limit. At the other location all concentrations could be quantified. Only at a few times the 6-hour concentrations exceeded $10 \mu\text{g m}^{-3}$: once at the Valthermond location and twice at the Borgercompagnie location.

During the measuring period of 1986, the average concentration at both locations was $2.6 \mu\text{g m}^{-3}$ (one exceptionally high value was omitted). Although the field next to the automatic sampler in Valthermond was treated with 1,3-dichloropropene, there was no measurable increase in concentration of this fumigant on the days following fumigation. This can be explained by the fact that the automatic sampler was upwind of the treated field in this period. At the Borgercompagnie location, a concentration of $263 \mu\text{g m}^{-3}$ was measured once, on November 10 (period 12.00-18.00 Central European Time). Influence of a field treated around that date was unlikely, since similar meteorological conditions one day later did not result in a distinct concentration. The high concentration may have been caused by the application of fumigant in the vicinity at the time of sampling. It is not clear what may have caused the two other concentrations which exceeded $10 \mu\text{g m}^{-3}$.

The 6-hour concentrations of 1,3-dichloropropene [(Z)- plus (E)-isomer] measured in the autumn of 1987 at the two sampling locations are shown in Figure 3. The fractions of concentrations within several classes also given in this Figure. The percentages of the 6-hour concentrations measured at the Valthermond and Borgercompagnie locations that remained below $3.2 \mu\text{g m}^{-3}$ were 75% ($n=55$) and 91% ($n=81$), respectively. The percentages of the concentrations below the detection limit at these locations were 1% ($n=1$) and 4% ($n=4$), respectively. At the Valthermond location, the fraction of the 6-hour concentrations that exceeded $10 \mu\text{g m}^{-3}$ amounted to 11% ($n=8$). At the other location, no 6-hour concentrations of more than $10 \mu\text{g m}^{-3}$ were measured.

From mid-September until mid-October 1987, the concentrations of 1,3-dichloropropene measured in Valthermond did not exceed $3.3 \mu\text{g m}^{-3}$ (see Figure 3). In this period, the average 6-hour concentration amounted to $1.9 \mu\text{g m}^{-3}$. The higher average value of $8.4 \mu\text{g m}^{-3}$ for the period from end October to mid-November can be explained by the fumigation of a field next to the automatic sampler. On the day of application, October 28, concentrations of around $5.6 \mu\text{g m}^{-3}$ were measured. On October 30, the concentrations measured were between 0.9 and $1.4 \mu\text{g m}^{-3}$. These low concentrations were due to the treated field being downwind from the automatic

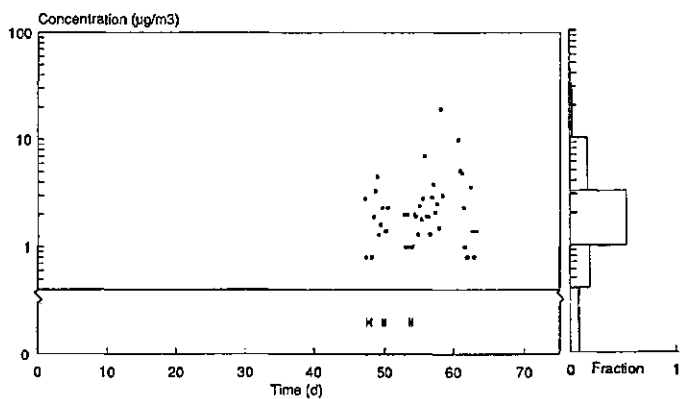
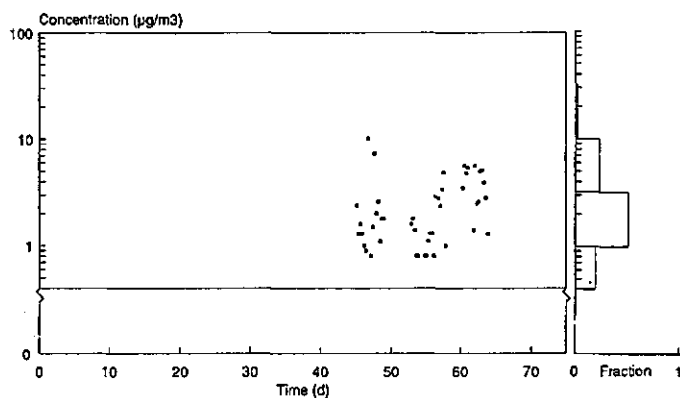


Fig. 2 6-Hour concentrations of 1,3-dichloropropene measured in the autumn of 1986 at the sampling locations of Bergercompagnie (top) and Valthermond (bottom). Zero time: September 15. Solid line=detection limit. Class boundaries at 0.4, 1.0, 3.2, 10 and 32 $\mu\text{g m}^{-3}$. — = period with concentrations below detection limit.

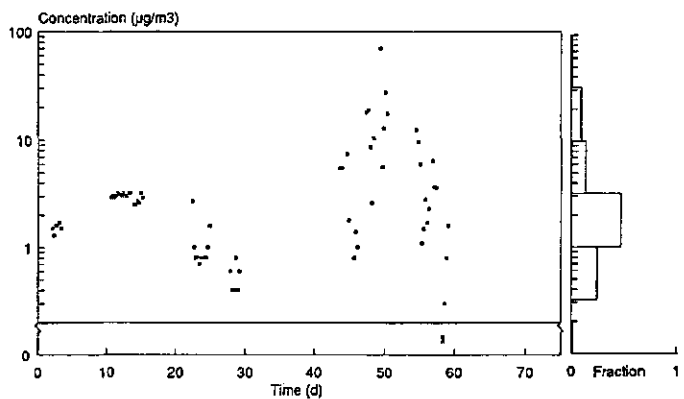
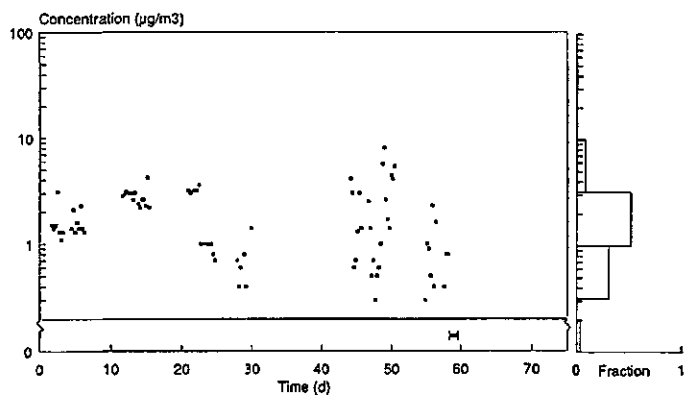


Fig. 3 6-Hour concentrations of 1,3-dichloropropene measured in the autumn of 1987 at the sampling locations of Borgercompagnie (top) and Valtiermond (bottom). Zero time: September 15. Solid line=detection limit. Class boundaries at 0.2, 0.32, 1.0, 3.2, 10 and 32 $\mu\text{g m}^{-3}$. --- =period with concentrations below detection limit.

sampler on that day. On November 1 the field was situated upwind of the automatic sampler, which caused concentrations to rise to $19 \mu\text{g m}^{-3}$. Concentrations ranging up to $28 \mu\text{g m}^{-3}$ were measured (with one exception of $71 \mu\text{g m}^{-3}$) on November 3 and 4. These comparatively high concentrations can be explained by the low wind speeds ($\leq 1.0 \text{ m s}^{-1}$) that prevailed when the air samples were taken. On November 11, the 6-hour concentrations of 1,3-dichloropropene in air were considerably lower: about $3.7 \mu\text{g m}^{-3}$. Presumably, the emission of the fumigant from the treated field next to the automatic sampler had decreased. On November 12, the concentrations decreased further to below $1.0 \mu\text{g m}^{-3}$, due to the prevailing higher wind speeds of between 6 and 11 m s^{-1} . From the beginning of the fumigation period (mid-September) until mid-October, the 6-hour concentrations measured in Borgercompagnie did not exceed $4.2 \mu\text{g m}^{-3}$. It is not clear why the concentrations measured in the period from November 2 to November 4 are higher than those measured on the previous or the following days. However, the wind speed for most of the time in that period was less than 1.5 m s^{-1} , which may have contributed to the differences. The average 6-hour concentration measured in the period from mid-September until mid-November was between 1.8 and $2.0 \mu\text{g m}^{-3}$.

3.2 Measurements of methyl isothiocyanate

The 6-hour concentrations of methyl isothiocyanate measured in the autumn of 1986 at the two sampling locations are shown in Figure 4. The fractions of concentrations within several classes also given in this Figure. During that autumn, 96% ($n=88$) of the 6-hour concentrations of methyl isothiocyanate were below the detection limit (for the 1986 measurements) of $2.0 \mu\text{g m}^{-3}$.

On September 21 (period 5.00-11.00 (a.m.) Central European Time), a comparatively high concentration of $96 \mu\text{g m}^{-3}$ was measured in Valthermond for which no explanation has been found. The next day under almost the same meteorological conditions, the 6-hour concentration for the same period was below $2 \mu\text{g m}^{-3}$. Again for the same period, a comparatively high 6-hour concentration of $6.1 \mu\text{g m}^{-3}$ was measured on September 23. However, there were no relevant treated fields within an upwind distance of 1.2 km. On later days, the 6-hour concentrations remained below the detection limit. At the other location, 95% ($n=20$) of the 6-hour concentrations were below the detection limit. Only once, there was a somewhat higher concentration of $3.2 \mu\text{g m}^{-3}$.

The 6-hour concentrations of methyl isothiocyanate measured in the autumn of 1987 at the two sampling locations are shown in Figure 5. The fractions of concentrations within several classes also given in this Figure. During that autumn, the limit of detection was reduced to $1.0 \mu\text{g m}^{-3}$, which enabled 48% ($n=49$) of the concentrations to be measured.

At the beginning of the fumigation period in 1987 (mid-September), the 6-hour concentrations ($n=6$) of methyl isothiocyanate measured in the air near Valthermond did not exceed the detection limit (for the 1987 measurements) of $1.0 \mu\text{g m}^{-3}$. During the end of September and the beginning of October many fumigations were done

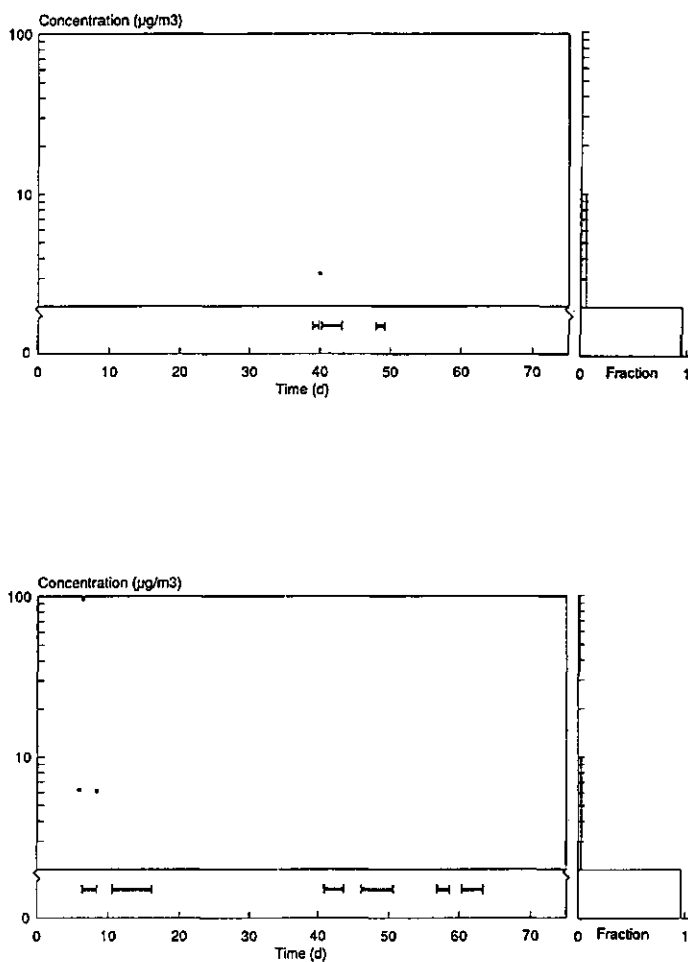


Fig. 4 6-Hour concentrations of methyl isothiocyanate measured in the autumn of 1986 at the sampling locations of Bergercompagnie (top) and Valkthermond (bottom). Zero time: September 15. Solid line=detection limit. Class boundaries at 2.0, 10 and 32 $\mu\text{g m}^{-3}$. --- =period with concentrations below detection limit.

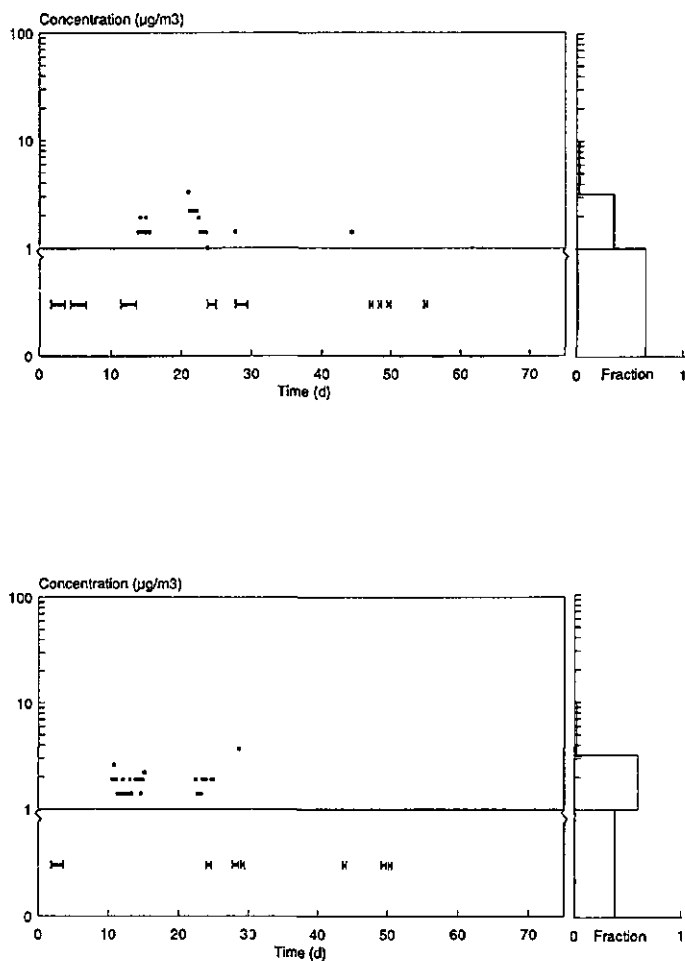


Fig. 5 6-Hour concentrations of methyl isothiocyanate measured in the autumn of 1987 at the sampling locations of Borgercompagnie (top) and Valthermond (bottom). Zero time: September 15. Solid line=detection limit. Class boundaries at 1.0, 3.2, 10 and 32 $\mu\text{g m}^{-3}$. — =period with concentrations below detection limit.

(see Table I). Nevertheless, the 6-hour concentrations hardly exceeded the detection limit: the average concentration was $1.7 \mu\text{g m}^{-3}$ ($n=25$). A treated field injected around October 2 about 0.35 km upwind from the automatic sampler may have influenced the 6-hour concentrations measured ($n=11$) during the period from October 7 to October 9: they ranged up to $1.9 \mu\text{g m}^{-3}$. As the weather became colder (first half of November), the 6-hour concentrations ($n=3$) dropped below the detection limit. In Borgercompagnie, the 6-hour concentrations measured ($n=58$), in general, hardly exceeded the detection limit. A treated field injected around October 2 about 0.15 km upwind from the automatic sampler may have influenced the 6-hour concentrations measured ($n=9$) in the period from October 5 until October 8: they were between 1.4 and $3.3 \mu\text{g m}^{-3}$. At Borgercompagnie too, the 6-hour concentrations ($n=4$) dropped below the detection limit in the first half of November.

3.3 Computed contribution from fields at various distances

The computed contribution to the concentration in air at the receptor site for a wind speed of 4 m s^{-1} under different atmospheric conditions of fields at various upwind positions in the simulated area of 10.0 by 10.5 km is presented in Figure 6. The concentrations calculated at the receptor resulting from the total of fumigations simulated were 4.0, 9.4, and $20.8 \mu\text{g m}^{-3}$ for Pasquill stability classes A, D and F, respectively. Under very unstable atmospheric conditions, only fumigations in the central W-E row close to the receptor were computed to contribute significantly to the concentration. In this row fumigations less than 1.5 km upwind from the receptor contributed to the concentration calculated at the receptor for more than 80%. Under neutral conditions, the contribution of fumigations farther away to the concentration in air at the receptor site was relatively higher. To comprise 80% of the concentration at the receptor site, the fumigated fields in the central W-E row of up to about 5 km in upwind direction needed to be taken into account. Under stable atmospheric conditions, a fumigated field in the central W-E row 7.5 km upwind was calculated to contribute 1% to the total concentration calculated at the receptor.

Fumigated fields at crosswind distances of more than 0.25 km were found to contribute only little to the concentration at the receptor. For fumigations in the W-E rows adjacent to that with the receptor, the maximum contribution under very unstable atmospheric conditions was computed to be 1% at an upwind distance of 0.5 km. From 0.5 km onwards, the contribution to the concentration at the receptor decreased gradually. The contribution of fumigations in the adjacent rows at upwind distances up to 1.5 km under stable atmospheric conditions was negligible, i.e. less than 0.1%. Outside this range, the contribution from fumigations in these rows reached 0.5% at a distance of 4 km remaining at this level for 5 km before decreasing (see Figure 6).

3.4 Computed concentrations of 1,3-dichloropropene

The contribution to the concentration at the receptor from the fumigated fields at upwind distances up to 1.0 km in both the W-E rows adjacent to the central row with

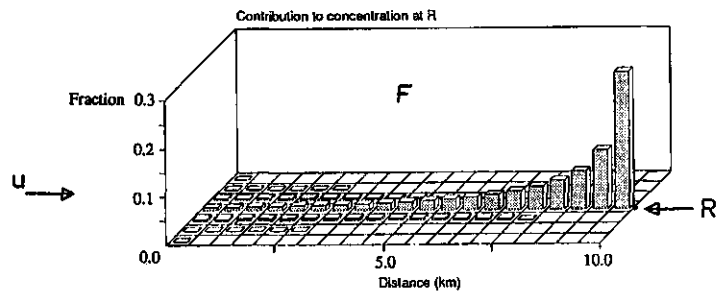
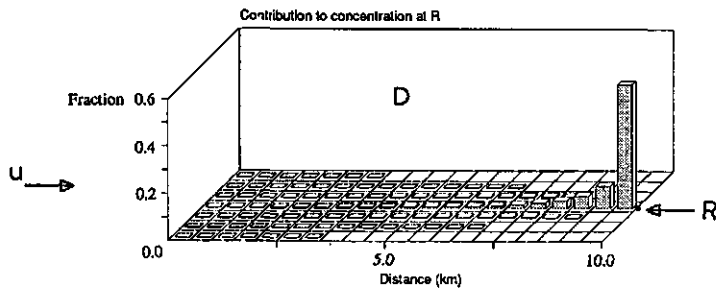
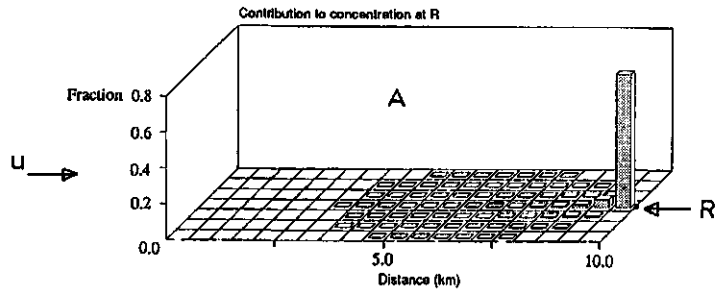


Fig. 6 Contribution of area sources (fields of 5 ha) located in squares of 0.5 by 0.5 km to the concentration in air computed at receptor R with the PAL model. Contribution expressed in fraction of the concentration at the receptor. Pasquill stability classes A, D and F: very unstable, neutral and stable atmospheric conditions, respectively. Arrow with u =wind direction.

the receptor (at crosswind distances of 0.25 km; see Figure 1) was less than $0.03 \mu\text{g m}^{-3}$. At upwind distances greater than 1.0 km, a change in the position of the fumigated fields in those rows did not affect the concentration at the receptor very much: their contribution ranged from 0.05 to $0.09 \mu\text{g m}^{-3}$. Contrastingly, a change in the position of the fumigated field in the central row significantly influenced the concentration at the receptor. The influence of distance on the concentration at the receptor is shown in Figure 7. The concentration of 1,3-dichloropropene [(Z)- plus (E)-isomer] at the receptor decreased from 9.90 to $0.21 \mu\text{g m}^{-3}$ when the upwind distance of the fumigated field increased from 0 to 5 km. The decrease in concentration was greatest when the upwind distance was increased from 0 to about 0.5 km. Outside that range, a more gradual decline in the concentration with increasing upwind distance was calculated.

The average value of $3.3 \mu\text{g m}^{-3}$ (ranging from 0.3 to $8.3 \mu\text{g m}^{-3}$) for the 6-hour concentrations of 1,3-dichloropropene ($n=11$) measured at Borgercompagnie in the week simulated, was within the range shown in Figure 7. The 6-hour concentrations of 1,3-dichloropropene ($n=9$) measured at the Valthermond location ranged from 2.7 to $28 \mu\text{g m}^{-3}$ (with one exception of $71 \mu\text{g m}^{-3}$). During part of the time of the simulated week, a field treated about 5 days before the beginning of this week was situated upwind from the measuring point at the Valthermond location. The higher concentrations were measured when wind speeds were lower than that introduced into the model.

Under neutral atmospheric conditions, frequently reported to occur in the autumns of 1986 and 1987,^{4,5} fumigated fields situated at locations in upwind direction from the receptor at distances up to a few km will contribute most to the concentration

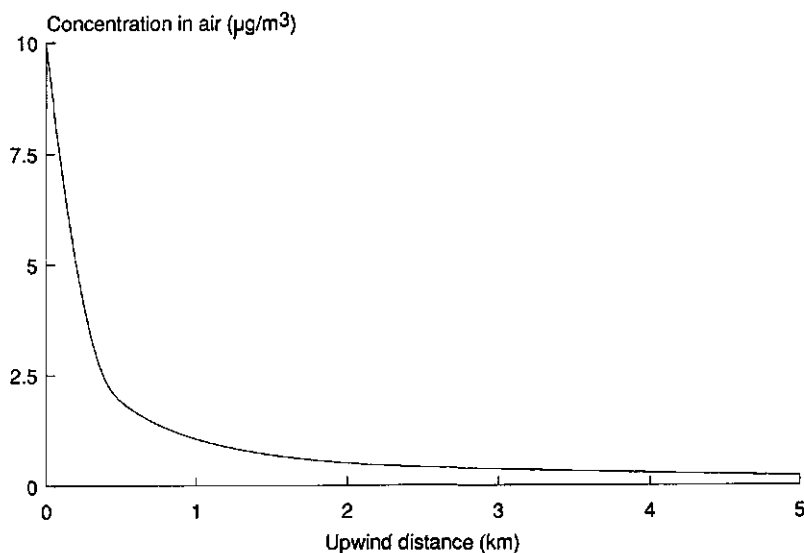


Fig. 7 Concentration of 1,3-dichloropropene in the air computed at the receptor site for various upwind distances between receptor and fumigated field in the central row.

in air measured at the receptor. Comparatively high 6-hour concentrations measured may indicate the presence of a treated field within this distance.

3.5 Computed concentrations of methyl isothiocyanate

The emission of methyl isothiocyanate from fields in the rows adjacent to the row with the receptor (see Figure 1) contributed little to concentration in air at the receptor. At upwind distances of up to 1.0 km, the contribution of a fumigated field in those rows was less than $0.02 \mu\text{g m}^{-3}$ and for a fumigated field further upwind it ranged from 0.01 to $0.03 \mu\text{g m}^{-3}$. A change in the position of the fumigated field in the central row had a distinct influence on the concentration computed at the receptor, as shown in Figure 8. The concentration of methyl isothiocyanate computed at the receptor site decreased from 2.5 to $0.18 \mu\text{g m}^{-3}$, when the distance between the receptor and the fumigated field was increased from 0 to 5.0 km. Again, the computed concentration decreased sharply when the upwind distance was increased from 0 to about 0.5 km. Outside that range, the concentration of methyl isothiocyanate declined more gradually when the upwind distance was increased.

The average 6-hour concentration of methyl isothiocyanate measured at both locations in the week simulated was $1.5 \mu\text{g m}^{-3}$ ($n=27$), thus within the computed range. The comparatively high concentrations measured in air may have been due to a fumigated field being within a distance of a few km upwind from the measuring point. This is supported by the fact that in the vicinity of the Valthermond and the Borgercompagnie measuring points, there were fumigated fields at upwind distances of 0.35 and 0.15 km, respectively.

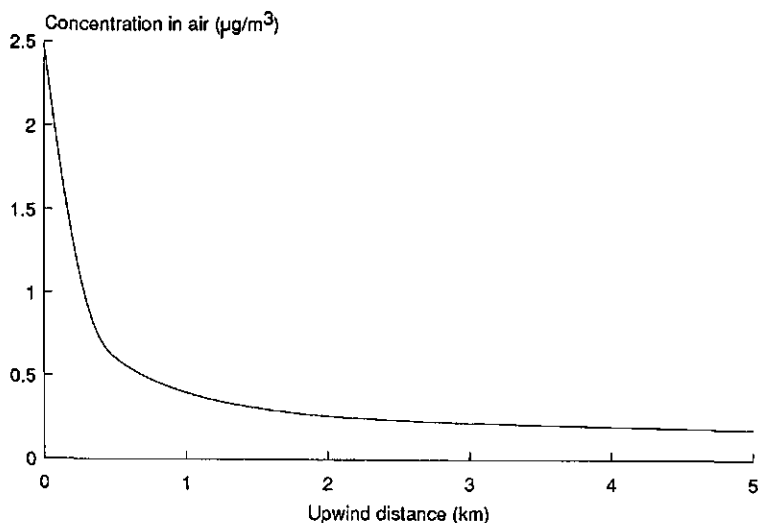


Fig. 8 Concentration of methyl isothiocyanate in the air computed at the receptor site for various upwind distances between receptor and fumigated field in the central row.

4 DISCUSSION AND CONCLUSIONS

Most of the 6-hour concentrations of 1,3-dichloropropene [(Z)- plus (E)-isomer] measured in 1986 and 1987 were below $3.2 \mu\text{g m}^{-3}$: 77% ($n=72$) and 84% ($n=136$), respectively. Only small fractions of the concentrations measured in 1986 (4%, $n=4$) and in 1987 (3%, $n=5$) were below the detection limits for the measurements in these years of 0.4 and $0.2 \mu\text{g m}^{-3}$, respectively. The fractions of the 6-hour concentrations measured in 1986 and 1987 exceeding a level of $10 \mu\text{g m}^{-3}$ were 3% ($n=3$) and 5% ($n=8$), respectively. For the concentrations exceeding $10 \mu\text{g m}^{-3}$ in 1986, no clear explanation could be given. The concentrations exceeding $10 \mu\text{g m}^{-3}$ in 1987 could be explained by a fumigation just upwind of the automatic sampler.

Almost all (96%, $n=88$) of the 6-hour concentrations of methyl isothiocyanate measured in 1986 were below the detection limit of $2 \mu\text{g m}^{-3}$. A small fraction (3%, $n=3$) of the concentrations measured were between 3.2 to $10 \mu\text{g m}^{-3}$ and only once a concentration exceeding $10 \mu\text{g m}^{-3}$ was measured. In the autumn of 1987, due to the lowering of the detection limit to $1.0 \mu\text{g m}^{-3}$, a larger fraction (48%, $n=49$) of the air samples taken could be quantified as compared to the samples taken in the autumn of 1986. In this year, 46% ($n=47$) of the 6-hour concentrations of methyl isothiocyanate measured ranged between 1.0 to $3.2 \mu\text{g m}^{-3}$ and 2% ($n=2$) between 3.2 to $10.0 \mu\text{g m}^{-3}$. Several comparatively high concentrations could be attributed to fumigations upwind of the sampling site, but for others no explanation could be found.

In general, the concentrations measured for methyl isothiocyanate were lower than those measured for 1,3-dichloropropene, in spite of the fact that more fields were treated with metham-sodium than with 1,3-dichloropropene. Presumably, the rate of emission of methyl isothiocyanate is lower than that of 1,3-dichloropropene, as has been estimated by van den Berg and Leistra⁷ using a computer-simulation model for the behaviour of fumigants in soil.

The concentrations of 1,3-dichloropropene in air reported in this study are all much lower than the maximum acceptable concentration of $5\,000 \mu\text{g m}^{-3}$ for occupational exposure adopted in the Netherlands.¹ However, little research has been published on possible adverse effects on human health caused by chronic exposure to concentrations of 1,3-dichloropropene in air below this level.¹³ For methyl isothiocyanate, no data have been found in the literature on adverse effects of this fumigant on human health by inhalation.

Little information has been found in the literature on concentrations of 1,3-dichloropropene and methyl isothiocyanate in air occurring in other regions where fumigations are done frequently. Albrecht and Chenchin¹⁴ took 40 L air samples (at a rate of 6 L h^{-1}) with charcoal tubes in a region where 1,3-dichloropropene is used for nematode control in pineapple culture. They measured concentrations of 1,3-dichloropropene of about $5 \mu\text{g m}^{-3}$ (at 1.0 m above the ground), but they did not present detailed information on fumigations upwind of the measuring point.

As expected, the highest concentrations of fumigant in air were measured when a field was fumigated just upwind of one of the automatic samplers. In a study on concentrations of 1,3-dichloropropene in air after injection (dosage 293 L ha⁻¹) into the soil (at 26 °C) at a depth of 0.45 m, Albrecht and Chenchin¹⁴ took 40 L air samples (at a rate of 6 L h⁻¹) with charcoal tubes. During the first few days after injection, concentrations of up to 3 000 µg m⁻³ were measured at 1.0 m above the treated soil surface. The concentrations in air found in this study, when a field was fumigated just upwind of an automatic sampler, were not as high as those measured by Albrecht and Chenchin¹⁴. Differences in soil and weather conditions are likely to have contributed to the difference. For example, the rate of emission can be expected to increase when the soil temperature increases and the soil moisture content decreases.

Computations using a model for fumigant dispersion in air showed that concentrations measured at a receptor site strongly depend on the stability of the atmosphere. It was found that under neutral atmospheric conditions and a moderate wind speed, fumigated fields within a distance of several kilometres upwind from the receptor site contributed most to the concentration at that site. Outside this range, their contribution decreased to below 1% of the concentration at the receptor site. However, under stable conditions the contribution of a fumigated field at an upwind distance of 7.5 km was still 1%. Contributions of fumigations at crosswind distances of 0.25 km or more were comparatively small, their contributions were about or less than 1%. Janni¹⁵ used another EPA dispersion model (PTDIS) for air pollutants, which is also based on the gaussian plume concept. His computations also showed that the stability condition is an important factor. The ground-level concentrations in air at a distance of 5 km downwind from the point source was computed to increase with a factor of about 250 when the stability type changed from A to F.

For a week in the beginning of November, when there was a comparatively high 1,3-dichloropropene usage, the concentration of 1,3-dichloropropene in air was calculated. Under meteorological conditions approaching the actual conditions in that week, the concentration in air for a simulated area with representative fumigations was calculated to be 9.9 µg m⁻³ on the downwind edge of a treated field. The computed concentration in air decreased sharply when the distance between the field and the receptor increased to 0.5 km. When the distance increased further, the computed decrease in the concentration was more gradual. Although the effect of fumigations in the region studied on fumigant concentrations in air was described in a very simplified way, the computed and measured concentrations of the fumigants in air were of the same order of magnitude.

The concentration of methyl isothiocyanate in air was calculated for a week in the beginning of October, when many applications with metham-sodium were done. Under meteorological conditions comparable to those during that week, the concentration in air for a simulated area with representative fumigations was calculated to be 2.5 µg m⁻³ at a receptor on the downwind edge of a treated field. When the distance between the field and the receptor site increased, a decrease of the concentration in air similar to that of 1,3-dichloropropene was calculated. Here again, despite the simplifications in the procedure to compute concentrations of this

fumigant in air, the computed and measured concentrations of the fumigants in air were of the same order of magnitude.

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SUMMARY AND CONCLUSIONS

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In the Netherlands, the fumigant 1,3-dichloropropene and the fumigant precursor metham-sodium are used on a large scale for nematode control in arable farming. These chemicals are usually injected at a soil depth of between 0.15 and 0.20 m. After their injection, a fraction of the dosage of the 1,3-dichloropropene and methyl isothiocyanate (formed from metham-sodium) diffuses up to the soil surface and escapes into the air. Because of their volatility, questions arose on the concentrations of 1,3-dichloropropene and methyl isothiocyanate in air around fumigated fields. As little information was available on the concentrations of these fumigants in air, a research programme was started to study the extent and significance of the emission of fumigant into the air after injection of the fumigant, or the fumigant precursor, into the soil.

A survey is presented of the processes and factors involved in fumigant behaviour in soil, and mathematical expressions for the processes were formulated (Chapter 2). Important processes are the transformation of fumigant in soil, the partitioning of fumigant between the soil phases and the diffusion of fumigant through the gas phase of the soil system. Convection of the gas phase in soil does not seem to contribute much to the transport of fumigant in homogeneous soils of medium or fine texture. However, it may be relevant in dry, coarse soils or in loosely-tilled topsoils containing large air voids. As the fraction of fumigant in the liquid phase is much higher than in the gas phase, transport of fumigant by convection in the liquid phase can be expected to be substantial in periods with net downward flux of liquid due to rainfall.

The partitioning of fumigant between the gas and liquid phases as well as the rate of transformation of fumigant in soil are substantially affected by soil temperature. The diffusion of fumigant through the gas phase depends on the volume fraction of that phase. Consequently, the flux density of fumigant diffusion in the gas phase is strongly affected by a change in soil moisture content due to rainfall or evaporation. Different soil and weather conditions during soil fumigations can be expected to result in large differences in the spread of fumigant in the soil.

A standard model to compute the spreading of fumigant in soil and its emission into the air after injection into the soil is described (Chapter 3). In this model, diffusion of fumigant in the gas phase was considered to be the only process in the transport of fumigant in soil. The formation of methyl isothiocyanate from metham-sodium and the transformation of 1,3-dichloropropene and methyl isothiocyanate were assumed to follow first-order kinetics. Constant soil moisture condition and temperature were assumed. Data on the input parameters were obtained from measurements in the laboratory or they were collected from the literature.

The standard model was used to simulate the fumigation of two fields injected with 1,3-dichloropropene and that of two other fields injected with metham-sodium (Chapter 3). The computed maxima in the rate of emission of 1,3-dichloropropene

into the air ranged from 24 to 178 $\text{mg m}^{-2} \text{d}^{-1}$ and were reached between 6 and 18 days after injection. Higher maxima were calculated for (Z)-1,3-dichloropropene than for (E)-1,3-dichloropropene and occurred sooner. The faster spreading of the (Z)-isomer in the soil is due to its higher volatility compared with the (E)-isomer. The computed maxima in the rate of emission of methyl isothiocyanate were 83 and 116 $\text{mg m}^{-2} \text{d}^{-1}$ and were reached at 6 and 3 days, respectively, after the injection of metham-sodium. For both 1,3-dichloropropene and methyl isothiocyanate, the computations showed that a up to a few tens of percent of the dosage can be lost by volatilization in the first three weeks following injection into the soil.

To check the computed spreading of fumigant in soil, the content profiles of the fumigant were measured in the soil of the four fields (Chapter 3). As soil samples were taken on a limited scale, only tendencies can be derived from the comparisons. In some cases substantial differences were found. For methyl isothiocyanate, the computed upward movement was higher than that measured. New data on content-dependent transformation kinetics were used to modify the submodel for the transformation of methyl isothiocyanate in soil. The content profiles computed with the modified model corresponded more favourably with the measurements.

A model for the behaviour of non-volatile pesticides in soil was modified by including descriptions of the diffusion of chemical compounds through the gas phase of the soil and the transfer of heat in soil (Chapter 3). The effect of rainfall and evaporation as well as that of diurnal changes in temperature on the rate of emission of fumigant into the air was estimated. Both factors were computed to affect the rate of emission of fumigant into the air substantially. However, a diurnally changing temperature resulted in a cumulative emission in time comparable with that computed for an isothermal soil system at the average temperature.

A procedure for sampling and analysis was developed to measure the concentrations of 1,3-dichloropropene and methyl isothiocyanate in air using charcoal as adsorbent (Chapter 4). In the laboratory, the influence of the sampling rate, sampling time and air humidity on the retention of fumigants on charcoal was investigated. The sampling and analytical procedure was tested by taking air samples during and after the injection of the fumigant, or the fumigant precursor, in a field and in greenhouse soil. The contents of the charcoal tubes were extracted with acetone and the extracts analysed by gas chromatography. The limits of detection, when sampling 40 L of air at a rate of 40 L h^{-1} , were 0.2 $\mu\text{g m}^{-3}$ for each isomer of 1,3-dichloropropene and 1.0 $\mu\text{g m}^{-3}$ for methyl isothiocyanate. The laboratory tests as well as the field tests showed that no breakthrough from the charcoal tube occurred when sampling at a rate of up to 60 L h^{-1} for one hour. Laboratory tests further showed that the charcoal tubes can best be stored at -20 °C and that storage time should not exceed four days.

Measurements on the concentration of methyl isothiocyanate in air were done around two fields after the soil had been injected with metham-sodium (Chapter 5). One-hour air samples were taken at a rate of 40 L h^{-1} (1.5 m above the ground). Using a gaussian plume model, the concentration patterns of methyl isothiocyanate in air around each field were computed for the times after injection at which air samples had been taken. The rate of emission into the air computed with the standard model

for fumigant behaviour in soil was taken as the source strength. Input data on the meteorological conditions were obtained from measurements in the field or from the nearest weather station. During the first few days after injection of the first field, the one-hour downwind concentrations measured ranged up to $3.1 \mu\text{g m}^{-3}$, whereas those computed for a height of 1.5 m ranged up to $4.7 \mu\text{g m}^{-3}$. During the period of 3 to 7 days after injection, the one-hour concentrations measured downwind of this field ranged up to $2.9 \mu\text{g m}^{-3}$, whereas those computed ranged up to $14 \mu\text{g m}^{-3}$. At sites downwind of the second field, one-hour concentrations of up to about $3 \mu\text{g m}^{-3}$ were measured one day after injection of metham-sodium. The computed concentrations downwind of the field were below $0.2 \mu\text{g m}^{-3}$. During the following eight days, the one-hour concentrations measured downwind of the field ranged up to $1.6 \mu\text{g m}^{-3}$, whereas those computed ranged up to $6.5 \mu\text{g m}^{-3}$. During the period of the first few days after injection of the second field, the lower downwind concentrations computed than those measured indicate that the actual rate of emission of methyl isothiocyanate from soil to air was higher than that computed with the standard model. For the first field such a difference was not found. In the subsequent period, up to seven to nine days after injection, the computed downwind concentrations for both fields tended to be higher than those measured. This may have been caused by an overestimation of the source strength of the emission. However, an increased dispersion in air due to obstacles near some of the sampling sites is likely to have contributed to the differences found, as in the model used to compute fumigant dispersion in air such obstacles were not taken into account.

Measurements on the concentrations of 1,3-dichloropropene in air were done around two fields after their injection with this fumigant (Chapter 6). One-hour air samples were taken at a rate of 40 L h^{-1} (1.5 m above the ground). The procedure to compute the concentrations of 1,3-dichloropropene in air around those fields was similar to that used to compute concentrations of methyl isothiocyanate in air around fields injected with metham-sodium. During the first three days after injection of 1,3-dichloropropene into the soil of the first field, the one-hour downwind concentrations in air computed for a height of 1.5 m ranged up to $19 \mu\text{g m}^{-3}$, whereas those measured ranged up to $29 \mu\text{g m}^{-3}$. For the period from five to ten days after injection, the concentrations computed and those measured ranged up to 36 and $16 \mu\text{g m}^{-3}$, respectively. For the other field, the computed downwind concentrations in air ranged up to $0.6 \mu\text{g m}^{-3}$ during the first three days after injection, whereas those measured ranged up to $23 \mu\text{g m}^{-3}$. For the period from four to nine days after injection, the concentrations computed and those measured ranged up to 2.3 and $1.3 \mu\text{g m}^{-3}$, respectively. During the first three days after injection, the one-hour concentrations measured were higher than those computed for both fields. This indicates that the actual rate of emission of 1,3-dichloropropene from soil to air was higher than that computed with the standard model. During the subsequent period, up to nine to ten days after injection, the computed and measured concentrations were mostly at the same level.

In two consecutive years, concentrations of 1,3-dichloropropene and methyl isothiocyanate were measured in 6-hour air samples taken at two locations in a region with intensive use of soil fumigants, i.e. the northeast of the Netherlands (Chapter 7). Most (about 80%) of the concentrations of 1,3-dichloropropene in air were below

$3.2 \mu\text{g m}^{-3}$. A small fraction exceeded $10 \mu\text{g m}^{-3}$, and most of the high values could be attributed to a fumigation just upwind of the sampling point. About 75% of the methyl isothiocyanate samples were below the detection limit in the two years, 1.0 and $2.0 \mu\text{g m}^{-3}$, respectively. Only once was a concentration in air exceeding $10 \mu\text{g m}^{-3}$ measured.

Using the standard model for fumigant behaviour in soil as described in Chapter 3, the course in the rate of emission of 1,3-dichloropropene and methyl isothiocyanate into the air after injection of the fumigant, or the fumigant precursor, into the soil was computed for fields representative of the northeast of the Netherlands. For some weeks with many fumigations in this region, the concentration of fumigant in air at a receptor site, with representative fumigated fields at different upwind distances, was computed using a gaussian plume model. The computed concentrations were compared with the 6-hour concentrations measured (Chapter 7). The computed concentration of 1,3-dichloropropene in air ranged up to $9.9 \mu\text{g m}^{-3}$ and that of methyl isothiocyanate ranged up to $2.5 \mu\text{g m}^{-3}$. The computed and measured concentrations were of the same order of magnitude, though the effect of the fumigations in the region was described in a simplified way.

SAMENVATTING EN CONCLUSIES

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De grondontsmettingsmiddelen 1,3-dichloorpropeen en metam-natrium worden in Nederland op grote schaal in de akkerbouw gebruikt ter bestrijding van nematoden. Deze middelen worden meestal geïnjecteerd in de bodem op een diepte tussen 0.15 en 0.20 m. Na injectie diffundeert een gedeelte van de dosering van 1,3-dichloorpropeen en methylisothiocyanaat (gevormd uit metam-natrium) naar het oppervlak en vervluchtigt naar de lucht. Gezien de vluchtigheid van deze middelen werden vragen gesteld naar de concentraties van 1,3-dichloorpropeen en methylisothiocyanaat in de lucht rondom behandelde velden. Het gebrek aan informatie over de concentraties van deze middelen in de lucht was aanleiding om een onderzoekprogramma te starten naar de mate en de betekenis van de emissie van vluchtige grondontsmettingsmiddelen naar de lucht na injectie in de grond.

Een overzicht werd gegeven van de processen en factoren die betrekking hebben op het gedrag van grondontsmettingsmiddelen in de grond en wiskundige uitdrukkingen voor de processen werden gegeven (hoofdstuk 2). Belangrijke processen zijn de omzetting van het middel in de grond, de verdeling van het middel over de bodemfasen en de diffusie van het middel door de gasfase van het bodemsysteem. Convectief transport van het grondontsmettingsmiddel met de gasfase lijkt in homogene gronden met fijnere textuur niet erg belangrijk te zijn voor het transport van het middel in de grond. Dit proces kan mogelijk wel van belang zijn in droge, grofzandige gronden of in gronden met een losgewerkte bouwvoor. Gezien het feit dat de fractie van het grondontsmettingsmiddel in de vloeibare fase veel groter is dan de fractie in de gasfase kan convectief transport van het middel met de vloeibare fase aanzienlijk zijn in perioden met een door regenval veroorzaakt netto-neerwaarts water transport.

De verdeling van het grondontsmettingsmiddel over de gas- en vloeistoffase, alsmede de snelheid van omzetting van het middel in de grond, worden in belangrijke mate beïnvloed door de temperatuur. De diffusie van het middel door de gasfase hangt af van de volume fractie van deze fase. Dientengevolge wordt de fluxdichtheid van de diffusie van het grondontsmettingsmiddel door de gasfase in sterke mate beïnvloed door veranderingen in het vochtgehalte van de grond door regenval en verdamping. Het is te verwachten dat verschillen in bodem- en weersgesteldheid leiden tot grote verschillen in de verspreiding van grondontsmettingsmiddelen in de grond.

Een standaardmodel om de verspreiding van het grondontsmettingsmiddel in de grond en de emissie ervan naar de lucht na injectie van het middel in de grond te berekenen werd beschreven (hoofdstuk 3). In dit model werd aangenomen dat diffusie van het middel door de gasfase de enige wijze van transport door de bodem is. Ook werd aangenomen dat de vorming van methylisothiocyanaat uit metam-natrium en de omzetting van 1,3-dichloorpropeen en methylisothiocyanaat volgens een eerste-orde proces verlopen. Verder werd verondersteld dat de temperatuur en de vochttoestand van de grond constant waren. Invoergegevens voor het model werden verkregen door metingen in het laboratorium of werden uit de literatuur gehaald.

Het standaardmodel werd gebruikt om de ontsmetting van twee velden geïnjecteerd met 1,3-dichloorpropeen en die van twee velden geïnjecteerd met metam-natrium te simuleren (hoofdstuk 3). De berekende maxima voor de bronsterkte van de emissie van 1,3-dichloorpropeen naar de lucht varieerden van 24 tot 178 $\text{mg m}^{-2} \text{d}^{-1}$ en ze werden bereikt tussen 6 en 18 dagen na injectie. Hogere maxima werden berekend voor (Z)-1,3-dichloorpropeen dan voor (E)-1,3-dichloorpropeen en ze werden eerder bereikt. De snellere verspreiding van de (Z)-isomeer in de bodem wordt veroorzaakt door de grotere vluchtigheid van deze isomeer ten opzichte van de (E)-isomeer. De berekende maxima voor de bronsterkte van de emissie van methylisothiocyanaat naar de lucht bedroegen 83 en 116 $\text{mg m}^{-2} \text{d}^{-1}$ en ze werden respectievelijk 6 en 3 dagen na de injectie van metam-natrium bereikt. Voor zowel 1,3-dichloorpropeen als methylisothiocyanaat werd berekend dat de emissie van deze middelen naar de lucht gedurende de eerste drie weken na injectie kan oplopen tot enkele tientallen procenten van de dosering.

De gehalteprofielen van de grondontsmettingsmiddelen in de bodems van de vier proefvelden werden op beperkte schaal gemeten ter controle van de berekende verspreiding van deze middelen in de bodem (hoofdstuk 3). Gezien het beperkte aantal metingen kunnen alleen trends worden aangeduid bij de vergelijkingen. In enkele gevallen werden aanzienlijke verschillen gevonden. Het berekende opwaartse transport van methylisothiocyanaat was groter dan gemeten. Nieuwe gegevens over de afhankelijkheid van de snelheid van omzetting van dit middel van het gehalte in de grond werden gebruikt om het submodel voor de omzetting van methylisothiocyanaat in grond te veranderen. De gehalteprofielen berekend met het aangepaste model stemden beter overeen met de gemeten gehalteprofielen.

Een model voor het gedrag van niet-vluchtige pesticiden in de bodem werd aangepast door toevoeging van beschrijvingen voor het transport van een stof door diffusie in de gasfase en voor het transport van warmte in grond (hoofdstuk 3). Het effect van regenval en verdamping alsmede dat van een dagelijks temperatuurverloop op de bronsterkte van de emissie van grondontsmettingsmiddel naar de lucht werden geschat. De berekeningen wezen uit dat beide factoren een aanzienlijk effect hebben op de bronsterkte van de emissie. De berekende cumulatieve emissie in de tijd bij een dagelijkse temperatuurgang was echter vergelijkbaar met die voor een isotherm bodemsysteem met een gemiddelde temperatuur.

Een bemonsterings- en analysemethodiek met actieve kool als adsorbens werd ontwikkeld ter bepaling van de concentraties van 1,3-dichloorpropeen en methylisothiocyanaat in lucht (hoofdstuk 4). De invloed van het monsternamedebiet, de monsternameduur en de luchtvochtigheid op de retentie van deze stoffen door actieve kool werd bestudeerd in het laboratorium. De bemonsterings- en analysemethodiek werden getest door luchtmonsters te nemen gedurende en na de injectie van grondontsmettingsmiddel in de vollegrond en in kasgrond. De inhoud van de koolstofbuisjes werden geëxtraheerd met aceton en de extracten werden geanalyseerd door middel van gaschromatografie. De detectiegrenzen voor een bemonsterd luchtvolume van 40 L bij een debiet van 40 L uur^{-1} bedroegen 0.2 $\mu\text{g m}^{-3}$ voor elk van de isomeren van 1,3-dichloorpropeen en 1.0 $\mu\text{g m}^{-3}$ voor methylisothiocyanaat. De toetsen in het laboratorium alsmede die in het veld en in

de kas wezen uit dat er geen doorbraak optreedt van deze stoffen uit de koolstofbuisjes bij een monsternamedebiet tot 60 L uur^{-1} gedurende 1 uur. De toetsen in het laboratorium wezen ook uit dat de koolstofbuisjes het beste bewaard kunnen worden bij -20°C en dat de bewaarperiode niet langer moet zijn dan 4 dagen.

Metingen van de concentraties van methylisothiocyanaat in de lucht werden gedaan rondom twee met metam-natrium geïnjecteerde velden (hoofdstuk 5). Eén-uurs luchtmonsters werden genomen bij een monsternamedebiet van 40 L uur^{-1} (1.5 m boven de grond). Met behulp van een gaussisch pluimmodel werden de concentratiepatronen van methylisothiocyanaat in de lucht rondom beide velden berekend voor de perioden na injectie waarin luchtmonsters werden genomen. De fluxdichtheid van de emissie naar de lucht berekend met het model voor het gedrag van grondontsmettingsmiddelen in de bodem werd ingevoerd als de bronsterkte. Invoergegevens betreffende de meteorologische omstandigheden werden verkregen door metingen in het veld of verkregen van het dichtstbijzijnde meteostation. De gemeten benedenwindse één-uursconcentraties gedurende de eerste dagen na de injectie van het eerste veld liepen op tot $3.1 \mu\text{g m}^{-3}$, terwijl de berekende concentraties voor een hoogte van 1.5 m opliepen tot $4.7 \mu\text{g m}^{-3}$. Gedurende de periode van 3 tot 7 dagen na injectie liepen de gemeten één-uursconcentraties benedenwinds van dit veld op tot $2.9 \mu\text{g m}^{-3}$, terwijl de berekende concentraties opliepen tot $14 \mu\text{g m}^{-3}$. Voor het tweede veld liepen de één dag na injectie van metam-natrium gemeten één-uursconcentraties op plaatsen benedenwinds van het veld op tot ongeveer $3 \mu\text{g m}^{-3}$. De berekende benedenwindse concentraties waren lager dan $0.2 \mu\text{g m}^{-3}$. Gedurende de volgende 8 dagen liepen de gemeten één-uursconcentraties op plaatsen benedenwinds van het veld op tot $1.6 \mu\text{g m}^{-3}$, terwijl de berekende concentraties opliepen tot $6.5 \mu\text{g m}^{-3}$. De lagere berekende benedenwindse concentraties, vergeleken met de metingen, gedurende de eerste paar dagen na de injectie van het tweede veld zijn een aanwijzing dat de feitelijke bronsterkte van de emissie hoger was dan die berekend met het standaardmodel. Een dergelijk verschil wordt niet gevonden voor het eerste veld. In de daaropvolgende periode tot 7 à 9 dagen na injectie was er voor beide velden een tendens dat de berekende benedenwindse concentraties hoger waren dan de gemeten concentraties. Dit zou veroorzaakt kunnen zijn door een overschatting van de bronsterkte van de emissie. Opgemerkt dient te worden dat een toename in de dispersie in lucht door obstakels in de buurt van sommige meetpunten mogelijk tot de geconstateerde verschillen heeft bijgedragen, aangezien in het dispersiemodel geen rekening werd gehouden met dergelijke obstakels.

Metingen van de concentraties van 1,3-dichloorpropeen in lucht werden uitgevoerd rondom twee met dit middel geïnjecteerde velden (hoofdstuk 6). Eén-uurs luchtmonsters werden genomen bij een monsternamedebiet van 40 L uur^{-1} (1.5 m boven de grond). De werkwijze voor de berekening van de concentraties van 1,3-dichloorpropeen in de lucht rondom die velden was analoog aan die voor de berekening van concentraties van methylisothiocyanaat in de lucht rondom velden geïnjecteerd met metam-natrium. Gedurende de eerste drie dagen na injectie van 1,3-dichloorpropeen in de grond van het eerste veld liepen de berekende benedenwindse één-uursconcentraties voor een hoogte van 1.5 m op tot $14 \mu\text{g m}^{-3}$, terwijl de gemeten concentraties opliepen tot $29 \mu\text{g m}^{-3}$. Voor de periode van 5 tot 10 dagen na de

injectie liepen de berekende en gemeten concentraties op tot respectievelijk 36 en 16 $\mu\text{g m}^{-3}$. Voor het andere veld liepen de berekende benedenwindse één-uursconcentraties gedurende de eerste drie dagen na injectie op tot 0.6 $\mu\text{g m}^{-3}$, terwijl de gemeten concentraties opliepen tot 23 $\mu\text{g m}^{-3}$. Voor de periode van 4 tot 9 dagen na injectie liepen de berekende en gemeten concentraties op tot respectievelijk 2.3 en 1.3 $\mu\text{g m}^{-3}$. Voor beide velden waren gedurende de eerste drie dagen na injectie de gemeten één-uursconcentraties hoger dan de berekende concentraties. Dit wijst erop dat de feitelijke bronsterkte van de emissie van 1,3-dichloorpropeen vanuit de bodem naar de lucht hoger was dan berekend met het standaard model. Voor de daaropvolgende periode, tot 9 à 10 dagen na injectie, lagen de berekende en gemeten concentraties meestal op hetzelfde niveau.

In twee opeenvolgende jaren werden concentraties van 1,3-dichloorpropeen en methylisothiocyanaat gemeten in 6-uurs luchtmonsters genomen in een gebied in Nederland waar grondontsmettingsmiddelen op grote schaal worden toegepast, nl. in het noordoosten (hoofdstuk 7). Het grootste deel (80%) van de concentraties van 1,3-dichloorpropeen in lucht lag beneden 3.2 $\mu\text{g m}^{-3}$. Een kleine fractie van de concentraties lag boven 10 $\mu\text{g m}^{-3}$, waarvan de meeste verklaard konden worden door een ontsmetting net bovenwinds van het meetpunt. Ongeveer 75% van de methylisothiocyanaat concentraties lag beneden de detectiegrens in de twee meetjaren van respectievelijk 1.0 en 2.0 $\mu\text{g m}^{-3}$. Slechts één keer werd een concentratie gemeten hoger dan 10 $\mu\text{g m}^{-3}$.

Met behulp van het standaardmodel voor het gedrag van grondontsmettingsmiddelen in de grond zoals beschreven in hoofdstuk 3 werd het verloop van de bronsterkte van de emissie van 1,3-dichloorpropeen en methylisothiocyanaat naar de lucht in de tijd na de injectie van de betreffende grondontsmettingsmiddelen in de grond berekend voor velden die representatief zijn voor noordoost-Nederland. Voor weken waarin deze middelen veel toegepast werden in deze regio, werd de concentratie van grondontsmettingsmiddel in de lucht op een receptorpunt met representatieve ontsmettingen op verschillende bovenwindse afstanden berekend met behulp van een gaussisch pluimmodel. De berekende concentraties werden vergeleken met de gemeten 6-uursconcentraties (hoofdstuk 7). De berekende concentratie van 1,3-dichloorpropeen in lucht liep op tot 9.9 $\mu\text{g m}^{-3}$ en die van methylisothiocyanaat liep op tot 2.5 $\mu\text{g m}^{-3}$. De berekende en gemeten concentraties waren van dezelfde orde van grootte, niettegenstaande het feit dat het effect van ontsmettingen in de regio op een vereenvoudigde wijze was beschreven.

CURRICULUM VITAE

Frederik van den Berg werd geboren op 26 april 1956 te Heemstede. Hij volgde de Atheneum-B dagopleiding aan de Spaarne Scholen Gemeenschap te Haarlem en behaalde het diploma in 1974. Daarop aansluitend begon hij met de studie aan de Landbouwhogeschool te Wageningen in de richting Bodemkunde en bemestingsleer, oriëntatie Bodemschei- en natuurkunde. Voor zijn praktijktijd ging hij naar het Instituut voor Bodemkunde en Agrochemie te Budapest (Hongarije). Het doctoraal examen werd in 1981 behaald en omvatte de vakken Bodemscheikunde (hoofdvak), Wiskunde (bijvak), Microbiologie (bijvak) en Organische chemie (bijvak).

Rond 1984 was hij gedurende een jaar werkzaam aan de Landbouwhogeschool Paris-Grignon (Frankrijk), waar hij onderzoek deed naar de adsorptie van een herbicide aan verschillende adsorbentia.

In 1985 begon hij als wetenschappelijk onderzoeker aan het toenmalige Instituut voor Onderzoek van Bestrijdingsmiddelen te Wageningen, waar hij gedurende ruim vier jaar onderzoek verrichtte naar de omvang en betekenis van de emissie van grondontsmettingsmiddelen naar de lucht. Sinds 1991 is hij als wetenschappelijk onderzoeker werkzaam aan het Winand Staring Centrum (SC-DLO) te Wageningen in het kader van het Meerjarenplan Gewasbescherming.