Volatilization of tri-allate, ethoprophos and parathion measured with four methods after spraying on a sandy soil

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ABSTRACT

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At about eleven times after application of tri-allate, ethoprophos and parathion to a sandy soil, their rates of volatilization were determined with the aerodynamic method (AD), the Bowen-ratio method (BR), the theoretical-profile method (TP) and the Box method (B). The volatilization was highest for tri-allate and lowest for parathion. On the first day after application, the volatilization rate decreased sharply, but thereafter the decrease was more gradual. The differences in volatilization rate as determined with the AD, BR and TP methods were comparatively small. The rates determined with the Box method were mostly lower than those determined with the other methods.

Keywords: aerodynamic method, air quality, air sampling, Bowen ratio method, Box method, field experiment, gas chromatography, pesticide, polystyrene, theoretical-profile method, XAD

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Preface

In recent years, the environmental risks of the large-scale use of pesticides has become a matter of concern. As most pesticides are applied as a spray onto the soil or crop, a part of the dosage can be expected to volatilize during and after application. As information on the rate and the extent of the volatilization of pesticides was scarce, a research project was financed by the Dutch Ministry of Agriculture, Nature Management and Fisheries to collect data on the volatilization of pesticides after their application in the field.

The research was part of the research programme of the Multi-Year Crop Protection Plan as adopted by the Dutch Ministry of Agriculture, Nature Management and Fisheries. In the framework of this plan, research is being done on the rate and extent of emissions of pesticides into the environment during and after their application.

The experiment was done at the experimental farm at Vredepeel (Limburg Province) in April 1993. A bare sandy soil was sprayed with three pesticides with different physico-chemical properties, i.e. tri-allate, ethoprophos and parathion. In this report, the results are given on a) the course with time of the rate of volatilization of each pesticide after application and b) the comparison of the pesticide volatilization rates as determined with different methods.

Thanks are due to C. Huys and P. Geelen of the experimental farm for their permission to carry out the experiment at the farm and for their co-operation before and during the experiment. The help of J.H. Oude Voshaar of the DLO Agricultural Mathematics Group with the statistical analysis of the results of the experiment is gratefully acknowledged.

Woord vooraf

In de laatste jaren is er bezorgdheid ontstaan over de risico's van het grootschalige gebruik van bestrijdingsmiddelen voor het milieu. Aangezien veel bestrijdingsmiddelen worden toegediend door bespuiting van grond of gewas, kan verwacht worden dat een deel van de dosering zal vervluchtigen gedurende en na de toepassing. Omdat er weinig informatie beschikbaar was over de snelheid en mate van vervluchtiging van bestrijdingsmiddelen, werd door het Ministerie van Landbouw, Natuurbeheer en Visserij een onderzoeksproject gefinancierd om gegevens te verkrijgen over de vervluchtiging van bestrijdingsmiddelen na hun toepassing in het veld.

Het onderzoek maakte deel uit van het onderzoeksprogramma van het Meerjarenplan Gewasbescherming, zoals dat werd aangenomen door het Ministerie van Landbouw, Natuurbeheer en Visserij. In het kader van dit plan wordt onderzoek gedaan naar de snelheid en mate van emissie van bestrijdingsmiddelen naar het milieu gedurende en na hun toepassing.

Het experiment werd in april 1993 uitgevoerd op de proefboerderij te Vredepeel (Provincie Limburg). Een onbegroeide grond werd bespoten met drie bestrijdingsmiddelen met verschillende fysisch-chemische eigenschappen, te weten tri-allaat, ethoprofos en parathion. In dit rapport worden de resultaten gegeven over a) het verloop met de tijd van de snelheid van vervluchtiging van elk bestrijdingsmiddel na toepassing en b) de vergelijking van de snelheid van vervluchtiging van de bestrijdingsmiddelen bepaald met verschillende methoden.

Dank is verschuldigd aan C. Huys en P. Geelen van de proefboerderij voor hun toestemming om het experiment op de boerderij uit te voeren en voor hun medewerking voorafgaand en gedurende het experiment. We zijn J.H. Oude Voshaar van de DLO-Groep Landbouwwiskunde erkentelijk voor de hulp bij de statistische analyse van de resultaten van het experiment.

Summary

During the past ten years, the large-scale use of pesticides in agriculture has become a matter of increasing political and public concern. In arable farming, most pesticides are sprayed onto the soil or on the crop. After application, a fraction of the dosage of the pesticide volatilizes. Dispersion of pesticide in the air results in exposure of people living in the neighbourhood of the site of application, which may result in adverse health effects. Deposition of pesticides from air onto soil and water surfaces may result in adverse effects on terrestrial and aquatic organisms.

The rate of volatilization of pesticide from the soil surface may be expected to be influenced by its physico-chemical properties, such as vapour pressure and solubility in water. As information on the volatilization rate from soil surfaces was scarce, a field experiment was set up to collect data on the course with time of the volatilization of tri-allate, ethoprophos and parathion after spraying onto a bare sandy soil.

At 10 to 12 times after the application of the pesticides, the volatilization rate of each pesticide was determined with the aerodynamic (AD) method, the Bowen-ratio (BR) method, the theoretical profile (TP) method and the Box method. The concentrations of the pesticides in air were measured and data on meteorological parameters were collected, as required by each method. The rate of decline of the fraction of the dosage of each pesticide remaining in the topsoil was also measured.

The highest rates of volatilization were determined during the first few hours after application. In the first hour after application, the average hourly rates of volatilization of ethoprophos and parathion determined with the AD, BR and TP methods were 3.4 and 0.25% of the dosage, respectively. For tri-allate in the second hour, the average hourly rate of volatilization determined with these methods amounted to 2.4% of the dosage.

On the first and second days after the day of application of tri-allate and ethoprophos, the hourly rates of volatilization determined with the AD, BR and TP methods were of the order of a few tenths of percent of the dosage. At these days, the hourly rate of volatilization of parathion was about 0.1 times those of tri-allate and ethoprophos.

At the end of the first week after application, the hourly rates of volatilization of tri-allate and ethoprophos had decreased to a few hundredths of percent of the dosage. At that time, the hourly rates of volatilization of parathion were also about 0.1 times those determined for the other two pesticides.

Around noon on the 14th day after the day of application, the hourly rates of volatilization of tri-allate and ethoprophos had increased to about 0.1% of their dosages. At this time, the hourly volatilization rate of parathion amounted to a few hundredths of percent of the dosage. Presumably, the top few mm of the soil were comparatively moist around noon. Later this day, the soil surface dried up, which resulted in a substantial reduction of the rate of volatilization.

The percentages of the dosage of the pesticides lost by volatilization during the first two weeks after application were estimated. It was assumed that volatilization during night-time was negligible. As expected, the volatilization loss of tri-allate was highest, i.e. 29% of the dosage. The calculated volatilization losses for ethoprophos and parathion were about 24% and 4% of their dosages, respectively. At two weeks after application, substantial fractions of the pesticides remained in the topsoil (30 to 50% of the dosage), so continued loss by volatilization can be expected.

The differences in volatilization rates as determined with the AD, BR and TP methods were comparatively small. The volatilization rates of the pesticides determined with the Box method were on average 0.3 times those determined with the AD, BR and TP methods (excluding those from a comparatively dry soil surface), and these differences were significant. The comparatively small range in volatilization rate determined with the Box method indicates that the covering of the soil surface with the box attenuated the differences in weather conditions, thereby reducing the change in the rate of volatilization.

The measurements showed the rate of volatilization of tri-allate to be higher than that of ethoprophos. If the rate of volatilization would only be related to the vapour pressure, then ethoprophos would be the most volatile. Presumably, other factors play a part. Assuming the volatilization rate to be related to the pesticide concentration in the gas phase of the soil system, the ratio between the rate of volatilization of tri-allate and that of ethoprophos is calculated to be 3.8. This corresponds roughly to the average ratio of 2.3 as determined with the four methods.

Shortly after application, the pesticides are present in a thin film on the soil surface. In this period, the ratio between the volatilization rate of two pesticides could be related to their Henry coefficients. For ethoprophos and parathion, the initial ratio between their volatilization rates was higher than that between their Henry coefficients. As parathion was applied earlier, a substantial fraction of its dosage may have become adsorbed onto soil, thereby reducing volatilization.

Accurate data are needed on the physico-chemical characteristics of pesticides to explain the differences between their rate of volatilization. As vapour pressures and water solubilities of most pesticides are rather low, high standards need to be met to measure these characteristics accurately.

The hourly concentrations of tri-allate, ethoprophos and parathion in air at 1.5 m above the ground were highest shortly after application: 5.3, 2.9 and 0.6 $\mu g\ m^{-3}$, respectively. In the next two days, the concentrations in air decreased substantially. The concentrations of parathion were a factor 100 or more below the maximum acceptable concentration (MAC-value) for occupational exposure, so the health risk to people living nearby sites of application seems to be comparatively small. For ethoprophos and tri-allate, no MAC-values have been adopted yet.

In the present study, ethoprophos and tri-allate were sprayed onto the soil surface. Usually, these pesticides are incorporated into the soil directly after application. This will substantially reduce their volatilization rate and their concentrations in air.

Samenvatting

In de laatste tien jaar is de bezorgheid in de politiek en bij de bevolking over het grootschalige gebruik van bestrijdingsmiddelen toegenomen. In de akkerbouw worden de meeste middelen verspoten op de grond of op het gewas. Na de toepassing vervluchtigt een deel van de dosering. Verspreiding van het middel in de lucht leidt tot blootstelling van mensen in de omgeving van de toepassing, wat kan leiden tot nadelige gezondheidseffecten. Depositie vanuit de lucht op grond- en wateroppervlakken kan leiden tot nadelige effecten op terrestrische en aquatische organismen.

De snelheid van vervluchtiging van een bestrijdingsmiddel vanaf de bodem wordt mogelijk beïnvloed door zijn fysisch-chemische eigenschappen, zoals dampdruk en oplosbaarheid in water. Omdat informatie over de vervluchtiging vanaf de bodem schaars was, werd een veldproef opgezet om gegevens te verkrijgen over het verloop met de tijd van de vervluchtiging van tri-allaat, ethoprofos en parathion na bespuiting van onbegroeide zandgrond.

Op 10 à 12 tijdstippen na toepassing van de bestrijdingsmiddelen, werd de snelheid van vervluchtiging bepaald met de aërodynamische (AD) methode, de Bowen-ratio (BR) methode, de theoretische-profiel-(TP) methode en de Kapmethode. Voor elke methode werden de benodigde metingen van de concentraties van de middelen in de lucht verricht en meteorologische gegevens verzameld. De afname in de tijd van de restfractie van de dosering van elk middel in de toplaag werd ook gemeten.

De hoogste vervluchtiging werd gemeten in de eerste uren na toepassing. In het eerste uur na toepassing bedroeg de met de AD, BR en TP methoden bepaalde gemiddelde uurlijkse vervluchtiging van ethoprofos en parathion respectievelijk 3,4 en 0,25% van de dosering. Voor tri-allaat bedroeg de met deze methoden bepaalde gemiddelde uurlijkse vervluchtiging in het tweede uur 2,4% van de dosering.

Op de eerste en tweede dag na de dag van toepassing van tri-allaat en ethoprofos bedroeg de met de AD-, BR- en TP-methoden bepaalde uurlijkse vervluchtiging ruwweg enkele tienden procenten van de dosering. Op deze dagen was de uurlijkse vervluchtiging van parathion ongeveer 0,1 van die van de andere twee middelen.

Tegen het einde van de eerste week na toepassing, waren de uurlijkse snelheden van vervluchtiging van tri-allaat en ethoprofos afgenomen tot enkele honderdsten procenten van de dosering. De uurlijkse vervluchtigingssnelheden van parathion waren op die tijd ook circa 0,1 maal die bepaald voor de twee andere bestrijdingsmiddelen.

Rond het middaguur van de 14e dag na de dag van toepassing was de uurlijkse vervluchtiging van tri-allaat en ethoprofos toegenomen tot circa 0,1% van de dosering. Op deze tijd bedroeg de uurlijkse vervluchtiging van parathion enkele honderdsten procenten van de dosering. Waarschijnlijk waren de bovenste mm van de grond relatief vochtig rond het middaguur. Later op de dag droogde het grondoppervlak op, wat leidde tot een aanzienlijke afname van de vervluchtigingssnelheid.

De percentages van de dosering van de bestrijdingsmiddelen vervluchtigd in de eerste twee weken na toepassing werden geschat. Aangenomen werd dat de vervluchtiging 's nachts verwaarloosbaar was. Zoals verwacht was het berekende verlies voor tri-allaat het hoogst: 29% van de dosering. De berekende verliezen voor ethoprofos en parathion waren resp. ongeveer 24 en 4% van de dosering. Twee weken na toepassing resteerden nog aanzienlijke fracties van de middelen in de bovengrond (30 tot 50% van de dosering), zodat een verder verlies via vervluchtiging verwacht kan worden.

De verschillen in de vervluchtigingssnelheden, zoals die bepaald werden met de AD, BR en TP-methoden, waren relatief klein. De vervluchtigingssnelheid van de middelen bepaald met de Kapmethode was gemiddeld 0,3 maal die bepaald met de AD, BR, en TP-methoden (uitgezonderd die vanaf een relatief droog bodemoppervlak) en deze verschillen waren significant. De relatief kleine variatie in de vervluchtigingssnelheid bepaald met de kapmethode duidt erop dat de bedekking van het bodemoppervlak door de kap de verschillen in weerscondities beperkte, waardoor er minder verandering was in de vervluchtigingssnelheid.

De metingen toonden aan dat de vervluchtiging van tri-allaat hoger was dan die van ethoprofos. Als de vervluchtigingssnelheid alleen van de dampdruk afhing, dan zou ethoprofos de meest vluchtige stof zijn. Andere factoren spelen blijkbaar een rol. Als men aanneemt dat de vervluchtigingssnelheid gerelateerd is aan de concentratie van het middel in de gasfase van het bodemsysteem, dan is de verhouding tussen de vervluchtigingssnelheden van tri-allaat en ethoprofos 3,8. Dit komt ruwweg overeen met de verhouding van 2,3 bepaald met de vier methoden.

Kort na toepassing zijn de bestrijdingsmiddelen aanwezig in een dunne film op de bodem. Het quotiënt van de vervluchtiging van twee middelen zou dan gerelateerd kunnen zijn aan die van hun Henry-coëfficiënten. Voor ethoprofos en parathion was het initiële quotiënt van de vervluchtigingssnelheden hoger dan die van hun Henry-coëfficiënten. Daar parathion eerder werd toegepast, kan een belangrijk deel van de dosering geadsorbeerd zijn geweest aan grond, waardoor de vervluchtiging afnam.

Nauwkeurige gegevens over de fysisch-chemische eigenschappen van bestrijdingsmiddelen zijn nodig om de verschillen in vervluchtigingssnelheid te verklaren. Omdat dampdruk en wateroplosbaarheid van de meeste bestrijdingsmiddelen laag zijn, zijn de kwaliteitseisen voor nauwkeurige metingen van deze eigenschappen hoog.

De uurlijkse concentraties van tri-allaat, ethoprofos en parathion in de lucht op 1,5 m boven de grond waren het hoogst kort na de toepassing: respectievelijk 5,3, 2,9 en 0,6 $\mu g\ m^{-3}$. In de volgende twee dagen namen de concentraties in lucht aanzienlijk af. De concentraties van parathion lagen een factor 100 of meer beneden de maximale aanvaarde concentratie (MAC) bij beroepsmatige blootstelling, zodat het risico voor de gezondheid van omwonenden relatief klein lijkt. Voor ethoprofos en tri-allaat zijn nog geen MAC-waarden vastgesteld.

In deze studie werden ethoprofos en tri-allaat verspoten op het bodemoppervlak. Gewoonlijk worden deze middelen direct na toepassing ingewerkt in de bodem. Dit zal hun vervluchtiging en hun concentraties in lucht beduidend doen afnemen.

1 Introduction

The possible adverse effects of the use of pesticides on a large scale have become a matter of concern. A fraction of the dosage of the pesticides may be transported away from the target area and be deposited on surrounding surfaces. Another fraction volatilizes from soil and crop surfaces and enters the atmosphere. The emission into the air leads to exposure of the applicator and of people in the surroundings of the application to pesticides in the air through inhalation. Deposition on water and soil surfaces leads to exposure of aquatic and terrestrial organisms.

The rate of volatilization may be affected by the physico-chemical properties of the pesticide, such as its vapour pressure, its solubility in water and the coefficient for its adsorption onto the soil. Furthermore, the course with time of the volatilization rate could be affected by meteorological factors, such as rainfall, temperature, radiation and wind speed. Large differences in the rate and extent of pesticide volatilization from soil surfaces may be expected.

Several laboratory experiments have been done on the factors affecting the rate of volatilization of pesticide from bare soil. Spencer and Cliath (1974) measured the rate of volatilization of trifluralin from silt loam in column experiments (column length 0.1 m; diam. 0.05 m) under a moist nitrogen atmosphere at 30 °C. During the first hour, about 7.5% of the dosage (equivalent to 2 kg ha^{-1}) volatilized from wet soil (moisture content 30%), whereas volatilization from air-dry soil only amounted to about 0.1% of the dosage. About half the dosage volatilized within the first 8 h after application. Dörfler et al. (1991) measured the rate of volatilization of atrazine and lindane from a bare sandy soil in a volatilization chamber (volume 0.02 m^3) at 20 °C. A water-saturated air stream was drawn through the chamber at a speed of 0.05 m s^{-1}. The half-lives for volatilization of atrazine and lindane from moist soil (40% of maximum water content) were 143 and 2.7 d, respectively. For dry soil, the half-lives were 939 and 6.7 d, respectively. It is not clear whether the volatilization rate measured in the laboratory is representative for that under field conditions.

Different methods have been described to quantify the rate of volatilization of pesticides in the field. Parmele et al. (1972) described two methods, i.e. the aerodynamic method and the Bowen-ratio method, for the measurement of the volatilization flux densities of dieldrin and heptachlor above a corn crop. At about two months after application, the hourly rates of volatilization ranged from 0.001% of the dosage (early morning and late evening) to about 0.01% of the dosage (around noon). During the morning and around noon, there was good agreement between the volatilization rates measured with the different methods, but later in the afternoon, there was a difference of about 25% between the methods. Majewski et al. (1990) compared the rates of volatilization of chlorpyrifos, diazinon, lindane and nitrapyrin from a bare soil measured with five methods at 13 times during the first three days after application. There were no significant differences at the 95% confidence level between the rates determined with the different methods. However, for some comparisons the number of measurements was limited. As none of these methods can be used as a check on the actual volatilization rate and as no independent measurements were made on the items of the mass balance of the pesticides, there is uncertainty whether the data collected with these methods correspond to the actual volatilization.

Whang et al. (1993) measured the volatilization of atrazine, chlorpyrifos and fonofos from a bare soil with the theoretical profile method. During the first 4 d, with daily maximum temperatures between 12 and 21 °C, the percentages of the dosages lost by volatilization for these pesticides were 0.7, 7 and 18%, respectively. During the subsequent 22 d, volatilization rates were lower, with volatilization losses estimated to be 1.2, 5 and 9% of the dosage, respectively. At 26 d, residues in the top 0.01 m of the soil were measured to be about 25, 41 and 28%, so further loss by volatilization could occur. Majewski et al. (1993) measured the rate of volatilization of tri-allate from a bare clayey soil with the aerodynamic method after spraying at about 18 °C. Shortly after application, high volatilization rates were measured but they decreased sharply during the following hours. During the first 5 d, about 34% of the dosage of tri-allate was lost by volatilization. As about 63% of the dosage remained after 5 d, a continued loss by volatilization can be expected.

A field experiment was done to collect data on the rates of the volatilization of tri-allate, ethoprophos and parathion from a bare sandy soil under weather conditions prevailing in spring in the Netherlands. At 10 to 11 times during the first 14 d after application, the rate of volatilization of each pesticide was quantified with four methods. At those times, air samples were taken to measure the concentration of the pesticides in air at sites and at heights required by the methods. Relevant meteorological parameters, such as vertical gradients of wind speed and air temperature, were measured continuously. At four times after application, soil samples were taken to measure the rate of decline of each pesticide. Some data on the physico-chemical properties of the pesticides studied are given in Table 1.

An attempt is made to explain the volatilization rates of the pesticides from their physico-chemical properties. The contribution of volatilization to the mass balance of the pesticides is discussed.

Table 1 Physico-chemical properties of the pesticides at 25 °C. K_{om} = coëfficient for the adsorption on organic matter

Pesticide	Molecular mass (g mol^{-1})	Vapour pressure (mPa)	Water solubility (mg L^{-1})	K_{om} (L kg^{-1})	Henry coefficient (Pa m^3 mol^{-1})
Ethoprophos	242.3	46.5 (26 °C)[a]	800[c]	60[d]	0.015
Tri-allate	304.7	16[a]	4[a]	1164[d]	1.2
Parathion	291.3	1.3[b]	24[b]	1760[d]	0.016

[a] Tomlin, 1994; [b] Jury et al. 1983; [c] Van der Pas (personal communication, 1994); [d] RIVM, 1989, 1990 and 1991.

2 Materials and methods

2.1 Description of the field and application of the pesticides

The experiment was carried out in April 1993 on a field at the experimental farm at Vredepeel (Province of North Brabant). A few days before the application, the field had been ploughed and harrowed. On the harrowed soil surface two plots were marked: a rectangular surface of 80 m by 122 m (0.98 ha) for the aerodynamic and Bowen-ratio methods and a circular surface with a radius of 20 m (0.126 ha) for the theoretical profile method. The plots were divided into quadrants to make soil sampling easier. The nearest wind obstacle in the surroundings of the two plots was a house about 60 m southwest of the circular plot. The field situation is presented in Figure 1.

Soil samples were taken from the top 0.1 m layer to determine the granular composition. The organic matter content was measured to be 3.7%. The percentages of the mineral parts in the size fractions 0-2 µm, 0-16 µm and 16-2000 µm were 2.3, 4.3 and 92.0%, respectively. Heterogeneities in soil composition within the rectangular plot were visible. The colour of the soil surface in the 4th quadrant was not as dark as in the other quadrants, presumably as a result of a lower organic matter content.

At 2, 7 and 14 d after application, samples were taken from the upper layer of the soil (about 5 mm thick) to measure its moisture content. From each quadrant 10 subsamples were collected in plastic bags. Each soil sample was mixed in the laboratory. A fraction of the samples was weighed before and after drying at 105 °C for 24 h.

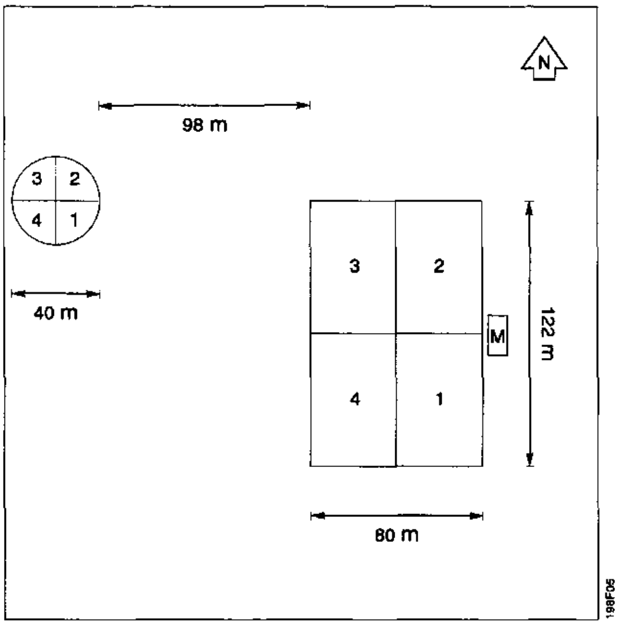

Fig. 1 Lay-out of the field experiment at Vredepeel in 1993. M = Meteorological station

At 7 d after application, soil samples were taken from the 0.00-0.05 m and 0.05-0.10 m layers to measure the volume fractions of the phases. The samples were taken with volumic rings (contents 100 cm^3) in each quadrant of both plots. The samples were weighed before and after drying at 105 °C for 24 h. It was assumed that the densities of the mineral and organic constituents were 2660 and 1470 kg m^{-3}, respectively.

The three pesticides were applied on April 6, 1993, using a Douven spraying machine. Its boom was equipped with five spraying segments with from one end of the boom to the other end of the boom 6, 9, 6, 9 and 6 ceramic Teejet spray nozzles (type XR 11001 VK). The total spraying width of the boom was 18 m. Before application, the rate of release of liquid from each nozzle of the spray boom was measured, while the tank of the spraying machine was filled with water. The liquid released from each nozzle in one minute was collected and weighed. At an adjusted pressure of 400 kPa the average release of liquid per nozzle was 1.78 ± 0.03 L min^{-1} (n = 36, s.d.= 0.03). The average driving speed, as measured over laps of 20 m, was 1.47 m s^{-1}. The total volume sprayed, as calculated from the average rate of release of liquid from the nozzles and the driving speed, was 0.402 m^3 ha^{-1}.

The pesticides were applied separately, because there was no information about interactions between the formulated pesticides upon mixing. The least volatile pesticide was applied first, i.e parathion. Thereafter, ethoprophos and triallate, respectively, were applied. The tank was filled with water to which an amount of the formulated product was added and then the spraying liquid was mixed. The volume of water transferred into the tank was measured using the water meter in the tank filling tube. Samples were taken from the formulated product, the spraying liquid in the tank and the spraying liquid as released from the outermost nozzle at the start and the end of the spraying. The samples were taken from the outermost nozzle to check whether the whole spraying system was filled with spraying solution. From these samples, 50 µl sub-samples were taken and extracted with 100 mL ethyl acetate by shaking for at least 15 min at 150 cycles min^{-1}.

The rectangular plot was sprayed in five tracks. Four tracks were sprayed with all nozzles of the boom spraying and one track was sprayed with only the nozzles of one side of the spray-boom functioning. The circular surface was sprayed by opening and closing each segment of the spraying boom at appropriate times.

For the application of parathion, the tank was filled with 575 L of water to which 10 L of Comchem parathion (0.25 kg parathion L^{-1}) was added and mixed by internal pumping. The tubes between the tank and the nozzles were rinsed with about 30 L of this spraying liquid. The application started at 10.15 h. First the circular plot was sprayed, directly followed by spraying of the rectangular plot. The application ended at 11.00 h. The volume of the spraying liquid remaining in the tank was about 100 L. The dosage was calculated to be 1.72 kg ha^{-1}.

For the application of ethoprophos, the tank was filled with 525 L of water to which 11 L of Mocap (0.2 kg ethoprophos L^{-1}) was added. Again, the tubes between the tank and the nozzles were rinsed with about 30 L of spraying liquid. The application started at 12.16 h. This time the rectangular plot was sprayed first, which was directly followed by the spraying of the circular plot. The application ended at 12.40 h. The volume of spraying liquid remaining in the tank was about 75 L. The dosage was calculated to be 1.66 kg ha^{-1}.

For the application of tri-allate, the tank was filled with 535 L of water to which 5 L of Avadex Bw (0.4 kg tri-allate L^{-1}) was added. Again, the tubes between the tank and the nozzles were rinsed with about 30 L of spraying liquid. The application started at 14.30 h with the spraying of the rectangular plot immediately followed by that of the circular plot. The application ended at 14.50 h. The volume of the spraying liquid remaining in the tank was 40 L. The dosage was calculated to be 1.48 kg ha^{-1}.

2.2 Determination of volatilization flux density

The flux density of volatilization of the pesticides from the soil surface was determined with four methods. Three of these methods were agro-meteorological methods, i.e. the aerodynamic method, the Bowen-ratio method and the theoretical-profile-shape method. Using these methods, the volatilization flux density is determined from measurements of the pesticide concentration in the air at one height above the centre of a circular treated plot or at different heights above the downwind edge of a sufficiently large treated plot. The fourth method was the Box method. With this method, the volatilization flux density of pesticide is measured directly at the soil surface.

2.2.1 Aerodynamic method

The aerodynamic method (AD) using the Thornthwaite-Holzman (TH) equation is a gradient method based on the logarithmic wind profile. In this method, the flux density of the emission of pesticide from soil to the air is proportional to the difference in the wind speed and that in the concentration of the pesticide in air at two heights above the downwind edge of the treated plot. A sufficiently large upwind fetch of one hundred times the highest measurement height is necessary. To account for the effect of atmospheric stability on the rate of volatilization of pesticide, the empiric expressions of Pruitt et al. (1973) were taken to calculate the correction coefficients of momentum and pesticide vapour. The stability parameter in these equations, the Richardson number, was determined by measuring the horizontal wind speed and the air temperature at two heights. The value for the von Kármán constant in the TH equation was taken to be 0.42. More details on this method have been given by Majewski et al. (1990 and 1991).

2.2.2 Bowen-ratio method

The Bowen-ratio method (BR) is based on the measurement of the energy balance at the soil surface. The terms in this balance are the net radiation (Rn), the soil heat flux (G), the latent heat flux (LE) and the sensible heat flux (H). The sensible heat flux can be calculated from measurements of the net radiation (Rn), the soil heat flux (G) and the ratio between the sensible and the latent heat flux, i.e. the Bowen-ratio. The Bowen-ratio is equal to the ratio between the air temperature gradient and the water vapour gradient, multiplied by the psychrometric constant (0.066 kPa $°C^{-1}$). From the calculated sensible heat flux and the vertical air temperature gradient measured, the exchange coefficient for sensible heat can be calculated. Further, it is assumed that this exchange coefficient is equal to the dispersion coefficient for the pesticide in air. The flux density of the volatilization of pesticide can now be calculated from the calculated coefficient of dispersion and the vertical concentration gradient of pesticide measured in air above the sprayed soil surface. For the BR-method, a sufficiently large homogeneous upwind fetch of one hundred times the highest measurement height is needed. This method has been described in more detail by Majewski et al. (1990).

2.2.3 Theoretical-profile-shape method

The Theoretical-profile-shape method (TP) is based on a trajectory simulation model for turbulent dispersion. For this method, the wind speed and the concentration of the pesticide in air need to be measured at a specific height above the centre of a circular plot. This height depends on the radius of the circle and the surface roughness of the plot and its surrounding area. The volatilization flux density of the pesticide can be calculated by multipying the wind speed with the concentration of the pesticide in air and by dividing it by the normalized flux density as predicted by the model. For the Vredepeel field and its surrounding area, the roughness length was estimated to be 0.03 m (Wieringa and Rijkoort, 1983). For a treated surface at this location with a radius of 20 m, the specific measurement height is 1.30 m and the normalized flux density is 6.0. The method has been described in detail by Majewski et al. (1989) and Wilson (1982).

2.2.4 Box method

A stainless steel box with a height of 0.1 m was placed on the sprayed soil surface. The soil surface covered by the box was 0.5 m by 2.0 m. Two aluminium pipes (length 2.0 m) were connected to the inlet and outlet sides of the box. The box was placed on the sprayed rectangular field near the upwind edge to avoid contamination of the inlet air by the pesticides. An air stream was drawn through the box at a rate of about 40 m^3 h^{-1}, which resulted in an air velocity within the box of 0.2 m s^{-1}. Subsamples from the outgoing air were taken to measure the mass of the pesticide volatilized.

2.2.5 Statistical evaluation of the methods

For each pesticide, statistical tests were done to check whether differences between the volatilization rates determined with the different methods were significant. For each pair of methods, the paired t-test was used on the logarithm of the volatilization rates as determined with these methods. Using the log-transformation, differences between methods on log-scale are tested, so on the original scale it is tested whether the ratio between the volatilization rates as determined with a pair of methods equals 1.0. If the P-value is less than 0.05, it is concluded that the volatilization rates as determined with this pair of methods differ significantly. The 95% confidence intervals of the ratio for each pair of methods were also calculated. The analysis was done with Genstat 5.3.1.

2.3 Meteorological measurements

The meteorological instruments were set up halfway the eastern side of the rectangular plot (See Figure 1). Rotating cup anemometers (Vector Instruments, type A100R) were mounted on a tripod at 0.30, 0.80, 1.30 and 2.00 m above the ground. A windvane (Vector instruments, type W200P) was attached at the end of a side arm at a height of 3.0 m above the ground. A lightning rod was mounted on the top of the pole and connected to a metal bar driven in the ground. On a second tripod, a casing with a cooled mirror dew point hygrometer and the datalogger (Campbell Scientific, type 21X) was mounted. Two air intakes, supported by metal arms (length 1.50 m), were placed at a height of 0.30 and 0.80 m above the ground and connected by plastic tubing to the dew point hygrometer (minimum accuracy 0.003 °C). Thermocouples of chromel-constantan wire (Campbell Scientific, type 107, minimum accuracy 0.01 °C) were put at the end of the supporting arms. At the top of this second pole, another lightning rod was placed. A Q^*6 net radiometer (Campbell Scientific) was installed at a few metres from the second pole and placed 1.0 m above the ground. Two soil heat flux plates (Campbell Scientific, type HFT-1) were installed at a depth of 0.08 m. The change in the average temperature of the top 0.08 m layer was measured by installing thermocouples close to each soil heat flux plate at soil depths of 0.02 and 0.06 m. The soil heat flux density at the soil surface was calculated from the heat flux density as measured at a depth of 0.08 m and the heat stored or released in the top 0.08 m. This heat was calculated from the heat capacity of soil (Q_s) and the change in the average temperature for this layer. The heat capacity of the topsoil during the period of the field experiment was estimated to be $1.47 \cdot 10^6$ J m^{-3} $°C^{-1}$.

All instruments were connected to the datalogger, which also controlled the instrument for water vapour measurement. The data collected were processed and subsequently stored. From the 10-s wind speed and wind direction measurements, 10-min averages were calculated. For the Bowen-ratio measurements, 20-min averages were calculated. The power for the datalogger was supplied by a car battery.

Additional data on the soil temperature were obtained by installing temperature probes (thermistors) at depths of 0.02 and 0.05 m. A rain gauge (Hellmann) with an electronical pulse counter was installed in the vicinity of the tripods. The surface area of the aperture was 200 cm^2. Each pulse signal corresponded to 0.25 mm of rainfall. The cumulative hourly rainfall data and hourly soil temperature data were collected with a datalogger (Tattle). The datalogger was installed on the first day after application.

2.4 Measurement of pesticides in air

2.4.1 Clean-up and recovery from adsorbent

The pesticide vapour was trapped on the polystyrene adsorbent XAD-4 (SERDOLIT^R, Serva, purity research grade). The particle diameter of the XAD-4 grains ranged from 0.3 to 1.0 mm. The size of the pores within the grains was 5 nm and the massic surface area of the XAD-4 grains was 750 m^2 g^{-1}.

As the XAD-4 contained impurities which interfered with the gas chromatographic analysis of the pesticides, a multiple extraction was carried out to remove these impurities. First, samples of 400 g dry XAD-4 were shaken with 500 mL ethyl acetate during 15 min and subsequently placed in an ultrasonic bath for 5 min. The solvent was removed using a Büchner funnel. After that, the adsorbent was subsequently shaken with acetone (300 mL), hexane (300 mL) and a mixture of ethyl acetate and acetone (150 mL; 1:1 v/v). Thereafter, the precleaned XAD-4 was extracted with Soxhlet on a water bath. A glass tube, closed at one side with a stainless steel wire netting (0.1 mm thick), was filled with precleaned adsorbent. The glass tube was placed in a 150 mL Soxhlet extractor, which was filled with a mixture of ethyl acetate and acetone (350 mL; 2.5:1 v/v). The contents of the glass tube were extracted for 20 h with approximately 6 cycles per hour. A second Soxhlet extraction was done with a mixture of hexane and acetone (400 mL; 1:1 v/v). The adsorbent was dried at about 30°C until it became odourless.

After cleaning the XAD-4, a check was made on the efficiency of the removal of the impurities. Samples of 10 g of the cleaned XAD-4 were shaken with 100 mL ethyl acetate for 30 min. A fraction of the extract was transferred to a Kuderna-Danish receiver with a 10 mL test-tube. The mass of the extract was measured (density of ethyl acetate 0.900 g mL^{-1} at 20 °C). The extract was concentrated to a volume of about 5 mL with a rotavapor. Thereafter, the receiver was placed in a water bath at 35 °C, where the extract was concentrated further under a nitrogen stream to a volume of about 1.0 mL. The mass of the concentrated extract was measured. Subsamples of the concentrated extracts were analysed with two gas chromatographic methods (See Section 2.4.4).

The retention of ethoprophos, tri-allate and parathion on XAD-4 was studied by drawing air through sampling tubes (length 70 mm, i.d. 35 mm, n = 3) with 10 g cleaned XAD-4 each, which had been spiked with 50 µl of an ethyl acetate solution containing 20 µg ethoprophos, 100 µg tri-allate and 10 µg parathion. A fourth sampling tube with 10 g XAD was connected to one of the spiked sampling tubes as check on breakthrough from that tube. The sampling tubes were connected to a high-volume vacuum pump (Siemens, type ELMO-G) and air was drawn for 1 hour at a rate of 3 m^3 h^{-1}. The ambient temperature and relative air humidity in this period were measured to be 17 °C and 45%, respectively. Thereafter, the contents of each tube was transferred into 250-mL glass flasks (type Schott) and to each flask about 50 mL ethyl acetate was added. The mass of ethyl acetate added to each flask was weighed. The flasks were shaken mechanically (150 cycles per min) during 30 min and then placed in an ultrasonic water bath for 10 min. About 1.5 mL of each extract was stored in deep freeze until analysis. The remaining extract in each flask was was concentrated as described above and subsequently stored in deep freeze until analysis.

The average masses of pesticide retained on XAD-4 were expressed as a percentage of the mass added. When analyzing the extracts without concentrating them, 104% (n = 3, s.d. = 0.5%), 99% (n = 3, s.d. = 1%) and 109% (n = 3, s.d. = 0.9%) were measured for parathion, tri-allate and ethoprophos, respectively. When the extracts were concentrated before analysis, the average masses retained were 96% (n = 3, s.d. = 1%), 87.6% (n = 3, s.d. = 1%) and 94% (n = 3, s.d. = 1%) for parathion, tri-allate and ethoprophos, respectively. Thus, the loss of pesticide during the concentration of the extract was comparatively small, i.e. about 10%.

2.4.2 Air sampling in the field

A special sampling head was constructed to sample the air in the field. It consisted of four parts, the first part being a conical glass tube (length 110 mm) with at one side an opening of 7 mm diameter and at the other side an opening of 35 mm diameter (Figure 2). The larger opening was provided with a screw thread (SVL 42) and it was connected to the glass sampling tube (length 70 mm, i.d. 35 mm) with a screw thread (SVL 42) at both sides. Inside the glass tube, a stainless steel wire-netting (mesh width 0.1 mm) was placed about halfway. This tube was provided with 10 g cleaned adsorbent (layer about 2 cm thick). At the top end of the sampling tube another glass tube was placed with the same dimensions as the sampling tube. The fourth part was an aluminium plate (10 cm by 10 cm) on a tripod which was placed on the upper glass tube to prevent rain drops falling into the tube. The tubes were connected to each other with a ferrule (PTFE) and a coupling unit to ensure the connection to be gastight (See Figure 2).

For the rectangular plot, the air sampling system consisted of a high-volume vacuum pump (Siemens, ELMO-G), a buffer vessel with a pressure valve (Alfa Laval), a manifold with five inlets and a manometer, five flow meters (Brooks Instruments, type 1307; max. flow rate 5 m^3 h^{-1}) and five gas meters (Schlumberger, type G 4-250; max. flow rate 6 m^3 h^{-1}). The sampling heads were connected to the pumping and air-flow system by stiff plastic tubing (i.d. 12 mm). A diagram of the air sampling system with its connections is given in Figure 3. The rate of sampling through each sampling head was adjusted to 3 m^3 h^{-1} with a restriction valve in the flow meters.

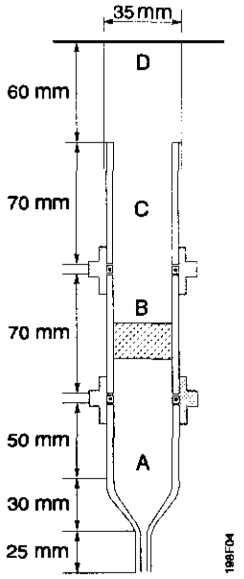

Fig. 2 Air sampling tube. A = conical glass tube. B = glass tube with XAD-4. C = glass tube. D = aluminium plate

The air was sampled at 0.30, 0.50, 0.80 and 1.50 m above the downwind edge of the treated field. Another glass tube filled with 5 g XAD-4 was connected to the bottom of the sampling tube at a height of 0.50 m above the ground, as a check on breakthrough.

The stainless steel box (length 2.0 m, width 0.5 m, height 0.10 m) was placed on the sprayed surface near the upwind edge of the sprayed rectangular surface. The air inlet was at about 2 m above the ground and air was drawn through the box at a rate of 40 m^3 h^{-1} (linear velocity about 0.2 m s^{-1}). Subsamples of the outgoing air were taken with three parallelly linked membrane vacuum pumps (KNF Neuberger) at an air-flow rate of about 2.7 m^3 h^{-1}. A gas meter (Schlumberger, type G 4-250; max. flow rate 6 m^3 h^{-1}) was used to measure the sampled air volume. The power for this system was supplied by a car battery.

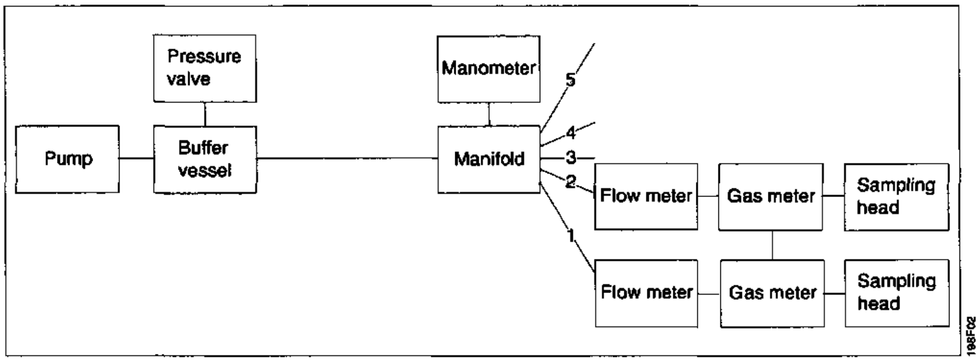

Fig. 3 Diagram of connections of the sampling unit

A second pumping and air-flow system was used for sampling the air above the circular plot. A high-volume pump (GAST) was used in combination with a manifold, three flow meters and three gas meters similar to those as described above. The manifold in this system had only three inlets. Two air samples per series were taken at a height of 1.30 m above the centre of the circular plot, at an air-flow rate of 4 m^3 h^{-1}.

At about 25 m upwind of each plot, air samples were taken at a height of 1.0 m above the ground to check for interfering compounds in the air and for upwind emissions of the pesticides applied in this study. For the rectangular plot, a vacuum pump (KNF Neuberger, type NO 135 ANE), a gas meter (Schlumberger, type G 4-250; max. flow rate 6 m^3 h^{-1}) and a vacuum control valve (Reichelt) were used. For the circular plot, a similar pumping system was used, but its capacity was somewhat higher. The rates of air sampling for the rectangular and circular plots were 4.5 and 5.5 m^3 h^{-1}, respectively.

At different times after application of the pesticides, air samples were taken. The first sampling period was directly after parathion had been applied. In this period, 1-hour air samples were taken only above the downwind edge of the rectangular plot. The next sampling period started about 15 min after ethoprophos had been applied. Again, 1-hour air samples were taken only above the rectangular plot. About one hour after the application of tri-allate, two more series of 1-hour air samples were taken above both the rectangular and circular plots. Simultaneously, four series of air samples were taken with the Box method for 0.5 hour. Between the second and third series, the box was moved a few metres to a new, undisturbed site. On the first and second days after the day of application, two series of 1-hour air samples were taken with each of the agro-meteorological methods and four series of 0.5-hour air samples were taken with the Box method. On the 7th and 14th day after the day of application, the duration of the sampling periods was doubled to two hours. From the first day after the day of application onwards, the box was moved a few metres to a new, undisturbed site after each second air sample. After sampling the tubes were closed with screw caps.

2.4.3 Extraction of the air samples

The air samples were extracted on the day at which they were taken. The XAD-4 in each tube was transferred to 250-mL Schott flasks and about 100 mL distilled ethyl acetate was added by weighing. The samples were extracted in the same way as those of the recovery experiment as described in Section 2.4.1. The extracts were stored for about 8 months in deep freeze before analysis. When the concentration of pesticide in the extract was below that in the lowest standard solution, the extract was concentrated as described in Section 2.4.1.

2.4.4 Gas chromatographic analysis

The concentrations of the pesticides in the extracts were measured using two methods. For ethoprophos, samples of 3 µl of the extracts were injected automatically into a gas chromatograph (Hewlett Packard type 5890) at 240 °C. The injection mode was splitless. A wide-bore fused-silica column (length 25 m; internal diameter 0.53 mm; film thickness 5.1 µm) with poly-siloxane (CP-Sil 5 CB) as stationary phase was used. The flow rates of the carrier and the make-up gases (both helium) were 10 and 20 mL min^{-1}, respectively. The initial column temperature was at 210 °C for 7 min. Thereafter, the temperature was increased at a rate of 45 °C min^{-1} to 260 °C and then maintained at this temperature for 3 min. The detector temperature was 280 °C. The flow rates of the detector gases hydrogen and medicinal air were 3.5 and 90 mL min^{-1}, respectively. Ethoprophos was measured with a thermionic nitrogen-phosporus detector. Data acquisition and processing were done with Multichrom (Fisons software). The retention time of ethoprophos under these conditions was 2.1 min. The detection limit in the samples ranged from 5 to 10 µg L^{-1}, which corresponded to concentrations of 2 to 4 ng m^{-3} in the air, when sampling air at a rate of 3 m^3 h^{-1} for 1 hour.

For tri-allate and parathion, samples of 3 µl of the extracts were injected automatically into a gas chromatograph (Hewlett Packard type 5890) at 240 °C. The injection mode was splitless. A medium-bore fused-silica column (length 25 m; internal diameter 0.25 mm; film thickness 1.2 µm) with poly-siloxane (CP-Sil 5 CB) as stationary phase was used. The flow rates of the carrier (helium) and make-up (nitrogen) gases were maintained at 2 and 58 mL min^{-1}, respectively. The initial column temperature was at 140 °C for 1.5 min. Thereafter, the temperature was increased at a rate of 45 °C min^{-1} to 250 °C and maintained at this temperature for 7 min. Finally, the temperature was increased at a rate of 45 °C min^{-1} to 290 °C and maintained at this temperature for 2 min. The detector temperature was 325 °C. Tri-allate and parathion were measured with a ^{63}Ni electron capture detector. Data acquisition and processing were done with Multichrom (Fisons software). The retention times of tri-allate and parathion under these conditions were 7.7 and 9.6 min, respectively. The detection limit in the samples ranged from 2 to 10 µg L^{-1} for tri-allate and from 5 to 10 µg L^{-1} for parathion. This corresponded to a concentration of tri-allate in the air of 1 to 4 ng m^{-3} and a concentration of parathion in the air of 2 to 4 ng m^{-3}, both at a sampling rate of 3 m^{-3} h^{-1} for 1 hour.

2.5 Measurement of pesticides in soil

2.5.1 Soil sampling and treatment in the laboratory

Four days before the pesticides were applied, samples were taken from the top 0.1 m layer of each quadrant of both plots. These soil samples were used for a check on residues of the pesticides from earlier applications.

At 0, 1, 7 (9 for the circular plot) and 14 d after application, soil samples were taken to measure the decline in the fraction of the dosage of each pesticide remaining in the soil. In each quadrant five sub-samples were taken with a trough (0.25 m by 0.10 m). At about 8 h after application only the top 0.03 m layer was sampled. On the first day after application, samples were also taken from the 0.03 - 0.06 m layer. At day 7 and 14 after the application, samples were taken from the 0.00 - 0.03, 0.03 - 0.06 and 0.06 - 0.10 m layers.

The samples were stored in deep freeze for about 5 months. Thereafter, the soil samples were defrosted, brought to room temperature and mixed for 10 min in a mixing machine (Hobart). Sub-samples were taken from the mixed soil samples to measure their moisture contents by measuring the loss of mass during drying at 105 °C for 24 h. The soil samples were put back into deep freeze until analysis.

2.5.2 Extraction and recovery

Samples of about 60 g of untreated moist soil from the top 0.10 m layer were weighed into 250-mL Schott flasks. Each sample was extracted by mechanical shaking (150 cycles per min) with a mixture of 50 mL ethyl acetate/hexane (1:1; v/v) and 50 mL distilled water for 30 min. After separation of the layers, the organic layer was collected in a test tube and centrifuged at 2000 rotations per min for 10 min. About 10 mL of the supernatant was transferred into a 20-mL flask and dried with anhydrous sodium sulphate. The dried extract was stored in deep freeze until analysis. The average contents of ethoprophos, tri-allate and parathion in untreated soil were below their detection limits of 0.004, 0.004 and 0.01 mg kg^{-1} (dry soil), respectively.

The efficiency of the method of extraction of the pesticides from soil was measured. Samples of about 60 g blank soil were taken and transferred into 250-mL Schott flasks. The mass of soil added to each flask was measured by weighing. Two of the samples were spiked with 1 mL of an ethyl acetate/hexane (1:1; v/v) solution of ethoprophos, tri-allate and parathion at a concentration of 300 mg L^{-1} for each pesticide. Three other samples were spiked with 1 mL of an ethyl acetate/hexane (1:1; v/v) solution containing 3 mg L^{-1} of each pesticide. The soil samples were mixed by rolling the flasks by hand and then they were stored at 5 °C for one night. After being brought to room temperature, the soil samples were extracted as described above. The fractions recovered at the 300 mg L^{-1} level were 101% and 99% for ethoprophos, 89% and 87% for tri-allate and 95% and 96% for parathion. For the spikes with a 3 mg L^{-1} solution of each pesticide, the fractions recovered were about 5-15% higher. The extractions were considered to be almost complete, so no corrections for the recovery percentage were applied to the measured values.

The soil samples taken after the application of the pesticides were extracted in the same way as the samples of blank soil.

2.5.3 Gas chromatographic analysis

The soil extracts were analysed with the gas chromatographic method using the nitrogen-phosphorous detector (See section 2.4.4). However, the programme to control the temperature of the column was changed to enable simultaneous analysis of ethoprophos, tri-allate and parathion. The initial column temperature was 100 °C for 1.5 min. Thereafter, the temperature was increased at a rate of 45 °C min^{-1} to 230 °C and then maintained at this temperature for 7 min. Finally, the temperature was increased at a rate of 45 °C min^{-1} to 260 °C and maintained at this temperature for 3 min. In this system, the retention times of ethoprophos, tri-allate and parathion were 5.5, 7.0 and 8.6 min, respectively.

3 Results

3.1 Meteorological and soil conditions

Results of the measurements of some characteristic meteorological parameters in the first 14 d after application are given in Figure 4A. During the application, the wind speed at 0.3 m was relatively high: 4.5 m s^{-1}. During the following two days, the wind speed decreased to about 1 m s^{-1}. On the third day after the day of application, the wind speed increased to 5 m s^{-1}, but it decreased again during the next day to 1 to 2 m s^{-1}. In the period between 4 and 10 d the wind speed was below 2.5 m s^{-1}, but at 12 d after application the wind speed increased to above 4 m s^{-1}.

The course with time of the air temperature as measured at 0.3 m above the ground is presented in Figure 4B. During day-time, the air temperature was mostly between 8 and 12 °C. However, during the 14th day after the day of application, the air temperature increased to about 23 °C. At the day of application and the first day thereafter, the daily amplitude of the air temperature was comparatively small, i.e. about 5 °C. From the second to the tenth day after the day of application, the daily amplitude was substantially higher, i.e. between 7 and 10 °C. On the 11th day after the day of application, there was hardly a difference between the air temperatures during day-time and those during night-time. Thereafter, the daily amplitude increased again to about 13 °C on the 14th day after the day of application.

The course with time of the net radiation as measured at 1.0 m above the ground is presented in Figure 4C. On the day of application, the maximum net radiation was about 220 W m^{-2}. On the following day, net radiation did not exceed 150 W m^{-2}. In the period from the second to the tenth day after the day of application, the daily maxima ranged mostly between 200 and 400 W m^{-2}. On the 14th day after the day of application, the maximum net radiation was as high as 500 W m^{-2}. During the night, the cooling of the soil resulted in a negative net radiation, but its absolute value was comparatively small.

The course with time of the soil heat flux density at a depth of 0.08 m is presented in Figure 4D. As expected, the soil heat flux density was positive (warming up of the soil by solar radiation) during day-time and negative during night-time. For the day of application and the following day, the daily maximum soil heat flux density did not exceed 40 W m^{-2}, but thereafter the daily maxima were mostly higher: they ranged between 40 and 100 W m^{-2}. The comparatively low heat flux density on the 11th day after the day of application is due to the low net radiation level on that day.

Data on the daily and cumulative rainfall during the first 14 d after application are presented in Figure 5. Between 10.00 and 18.00 h on the day of application 1.7 mm of rain was collected, part of which fell between the third and fourth sampling

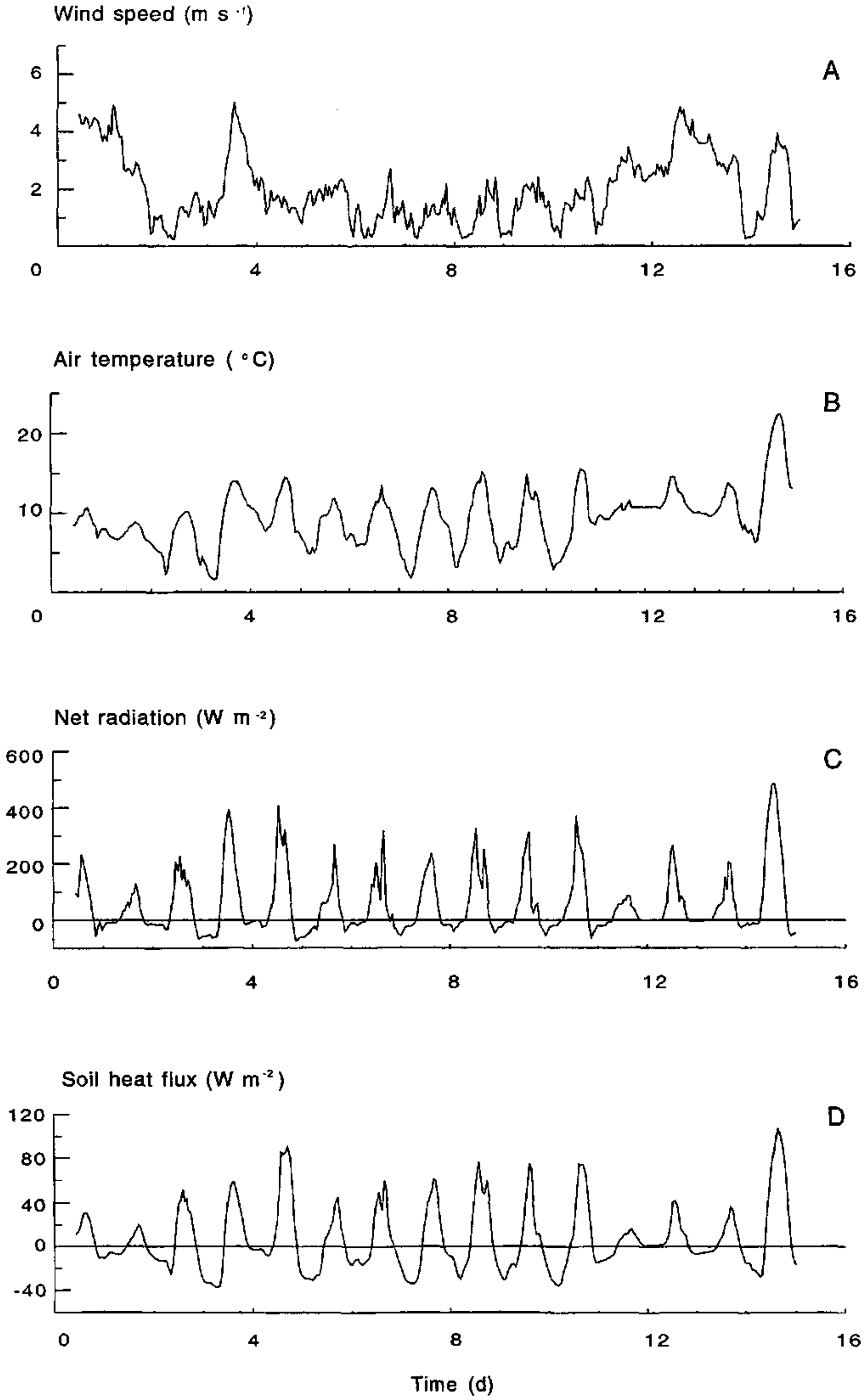

Fig. 4 Hourly average wind speed at 0.3 m above the ground (A), air temperature at 0.3 m above the ground (B), net radiation at 1.0 m above the ground (C) and soil heat flux at a depth of 0.08 m (D) at the Vredepeel field. Zero time = April 6, 1993, 0.00 h (Central European Summer Time)

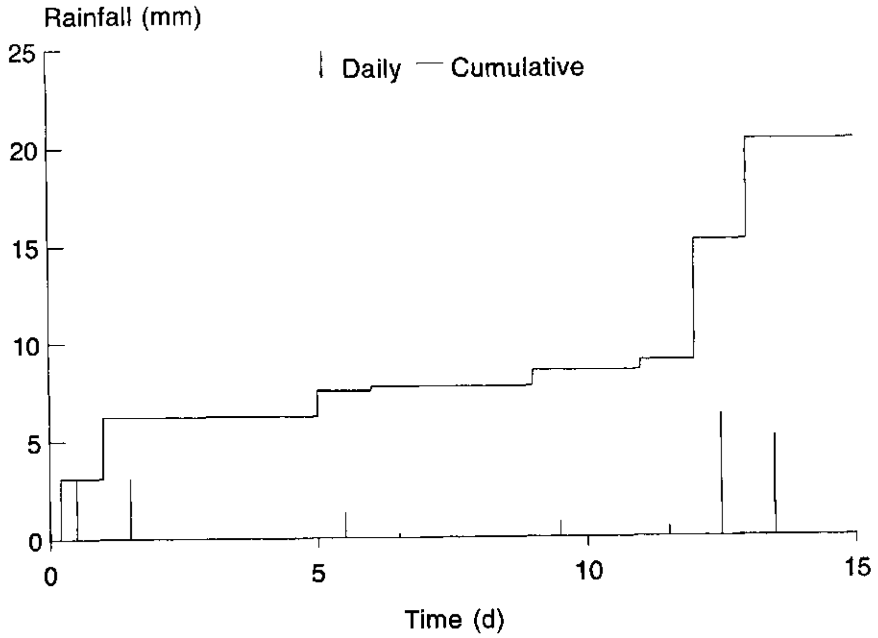

Fig. 5 Daily (bars) and cumulative (solid line) rainfall at the Vredepeel field. Zero time = April 6, 1993, 0.00 h (Central European Summer Time)

series (from 16.56 to 17.32 h). In the course of the evening it started to rain; the amount of rainfall during the next 20 hours was measured to be 4.5 mm. From the first to the 12th day after the day of application, the weather was mostly dry; a few mm of rainfall was measured on the 5th and 9th days after the day of application. On both the 12th and 13th days, about 5 mm of rain fell. On the next 2 d hardly any rainfall was recorded. The total amount of rainfall over 14 d was 20 mm.

On the 2nd (around 19.00 h), 7th (around 18.00 h) and 14th (afternoon) days after the day of application, the moisture content of the uppermost layer (about 5 mm thick) of the soil profile was 13, 5.0 and 4.7%, respectively. At 0, 1, 7 and 14 d after application, the moisture content in the soil samples taken from the top 0.03 m layer (See Section 2.5.1) were measured to be 16, 16, 8.5 and 11%, respectively.

3.2 Remaining fractions of the pesticides in the soil

The course with time of the fractions of ethoprophos, tri-allate and parathion remaining in the top 0.03 m layer of the soil of the rectangular plot is given in Figure 6. At about 0.3 d after application, the fraction of ethoprophos remaining was 67% of the dosage. During the following two weeks, its fraction remaining in the top 0.03 m layer decreased rather slowly. At 14 d after application, the remaining fraction of ethoprophos was measured to be 52% of its dosage. Using the first-order rate equation to describe the course with time of the measured fraction of ethoprophos remaining in the top soil layer, the best-fitting line was calculated for the percentage remaining (log scale) against time, using linear regression with the least-squares method. The half-life of ethoprophos was calculated to be 112 d.

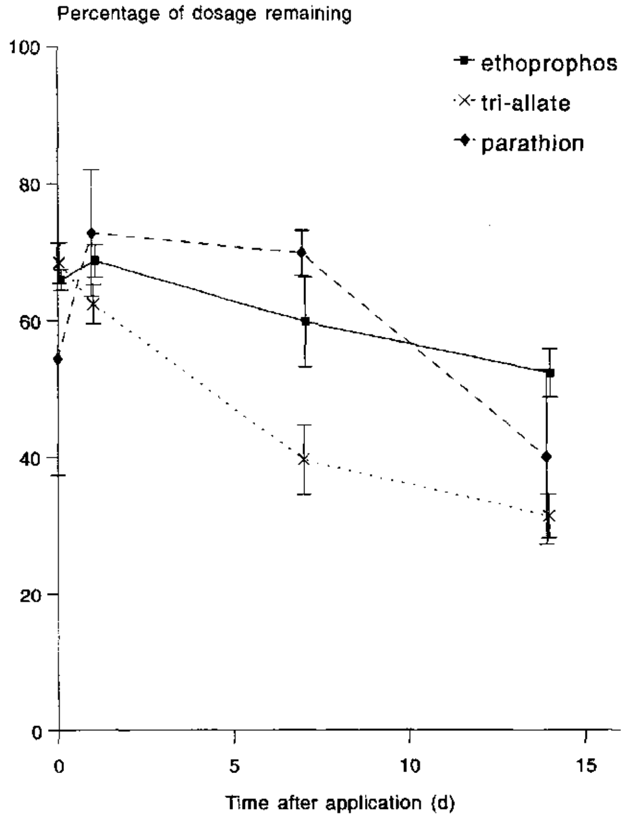

Fig. 6 Remaining fractions of ethoprophos, tri-allate and parathion in the top few cm of the soil after spraying of the Vredepeel field. Day of application: April 6, 1993. Ending times of the applications of parathion, ethoprophos and tri-allate were 11.00, 12.40 and 14.50 h, respectively

At about 0.3 d after application, the remaining fraction of tri-allate was measured to be 69% of the dosage. Thereafter, there was a clear decrease in the fraction of tri-allate remaining in the top few cm of the soil. At 14 d after application, the fraction remaining was 31%. The calculated half-life of tri-allate in the top soil layer was 37 d.

At about 0.3 d after application, the remaining fraction of parathion was 54% of the dosage. At one day after application, a higher fraction of parathion was measured to remain. Possibly, this difference is caused by variations in the areic deposition of parathion within the field resulting from variable drift and spray cone patterns, as caused by the strong wind (gusts) during the parathion application (wind speed at 0.3 m higher than 4 m s^{-1}). During the first week after application, the remaining fraction of parathion decreased hardly. Thereafter, the rate of decline of parathion in the soil increased. At 14 d after application, about 40% of the dosage remained.

3.3 Concentrations of the pesticides in air

The surface area of the rectangular plot is more representative for applications of pesticides under field conditions than that of the circular plot. Therefore, the concentrations of the pesticides in air measured at the downwind edge of the rectangular plot can be used best to discuss the concentration levels in air for field applications. The highest concentrations of the pesticides in air at the downwind edge of the rectangular plot were measured directly after application. For the second hour after the application of tri-allate, its concentration in air at a height of 1.5 m above the ground was 5.3 µg m^{-3}. About 1.5 h later, the 1-h concentrations in air had decreased by roughly a factor 2. During the afternoon of the next two days, the concentration of tri-allate in air at a height of 1.5 m above the downwind edge of the field (0.7 µg m^{-3}) was distinctly lower than that measured on the day of application. At 7 and 14 d after application, the concentration in air at a height of 1.5 m ranged from 0.04 to 0.25 µg m^{-3}.

During the first hour after the application of ethoprophos, the concentration of this pesticide in air at a height of 1.5 m above the ground at the downwind edge of the rectangular plot was measured to be 2.9 µg m^{-3}. During the following 5 hours, the 1-h concentration of ethoprophos in air measured at this height above the downwind edge had decreased to 1.2 µg m^{-3}. In the afternoon of the first and second days after the day of application, the concentration in air measured at a height of 1.5 m was about 0.5 µg m^{-3}. At 7 and 14 d after application, the highest concentration in air measured was about half that measured in the afternoon of the first few days after the day of application. On the 7th and 14th days after the day of application, the concentration in air measured at 1.5 m above the downwind edge decreased from 0.07 to 0.26 µg m^{-3} around noon to 0.02 µg m^{-3} late in the afternoon.

During the first hour after the application of parathion, its concentration in air at a height of 1.5 m above the ground at the downwind edge of the rectangular plot was measured to be 0.62 µg m^{-3}. During the following 6.5 hours, the 1-h concentration of parathion in air measured at 1.5 m above the ground decreased to 0.19 µg m^{-3}. In the afternoon of the first and second days, the 1-h concentrations of parathion in air measured at a height of 1.5 m above the downwind edge were about 0.09 µg m^{-3}. Around noon on the 7th day after the day of application, the concentration of parathion in air at a height of 1.5 m (0.02 µg m^{-3}) was even lower than that measured 5 d earlier. In the course of the afternoon, its concentration in air had decreased further to 0.005 µg m^{-3}. On the 14th day after the day of application, the range in concentrations measured at 1.5 m during the afternoon was higher than that measured on the 7th day: it ranged from 0.008 to 0.07 µg m^{-3}.

No air samples were taken during the first hour after the application of tri-allate. Its concentration in air during the first hour after application can be expected to have been higher than that measured during the second hour.

Almost all concentrations in air could be quantified. Only once, at 14 d after application, the concentration of parathion in air at 1.3 m above the centre of the circular plot was below the detection limit of 0.002 µg m^{-3}. More detailed data on the concentrations of tri-allate, ethoprophos and parathion measured in air at different heights above the rectangular plot are given in Annex 2, Table 1. Detailed data on the concentrations of these pesticides in air as measured above the centre of the circular plot are given in Annex 2, Table 2.

There was a linear relationship between the concentration of pesticide in air and the logarithm of the sampling height. As an example, the concentration profile of tri-allate in air above the soil surface of the rectangular plot is shown in Figure 7. The difference between the concentration of pesticide in air measured and that calculated for the same height by linear regression was mostly not more than 20%.

For the second series on the day of application (starting time 12.42 h), the concentrations of ethoprophos and parathion measured in air at a height of 1.5 m above the ground were higher than those measured at a height of 0.8 m above the ground. Presumably, an error has been made when collecting the samples in the field. When assuming the lower concentrations measured to originate from the sample taken at 1.5 m above the ground, again a linear relationship was obtained between the concentration in air versus the log (sampling height). Therefore, the sequence of theseconcentrations measured is reversed and this reversed sequence is given in Annex 2, Table 1.

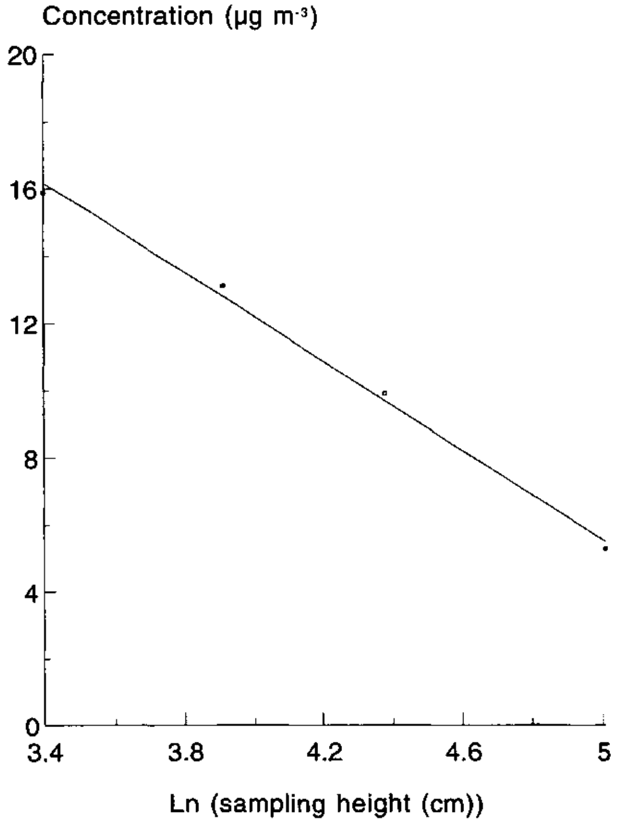

Fig. 7 Concentration profile of tri-allate in air calculated from measurements at four heights

3.4 Rates of volatilization of the pesticides

3.4.1 Rate of volatilization of tri-allate

The rates of volatilization of tri-allate from the soil, expressed as a percentage of its dosage per hour, as obtained with each method for 10 times after the application are given in Table 2. The corresponding areic rates of volatilization are presented in Annex 3, Table 1.

For the second hour after application, the average volatilization rate as determined with the agrometeorological methods amounted to 2.4% (n = 3; s.d. = 0.4) of the dosage. The hourly volatilization rate as determined with the Box method was lower: 1.1% of the dosage. About 1.6 h later, the average hourly volatilization rate as determined with the agrometeorological methods was 1.7% (s.d. = 0.6). Presumably, the cooling down of the soil surface towards the evening (See Figures 4C and 4D) resulted in lower rates of volatilization. Again, the hourly volatilization rate as determined with the Box method was lower: 0.7% of the dosage.

At 1.0 d after application (early afternoon), the average of the hourly volatilization rates of tri-allate as determined with the agrometeorological methods was 0.33% (s.d. = 0.08) of its dosage. Later in the afternoon, at 1.1 d after application, the hourly volatilization rate as determined with these methods was 0.26% (s.d. = 0.08). The lower volatilization rate can largely be explained by less mixing of pesticide vapour with air due to the lower wind speed gradient (AD method), the lower exchange coefficient of sensible heat (BR method) and the lower wind speed as measured at 1.3 m above the ground (TP method; See Section 2.2 and Annex 1). Further, the concentration gradient measured above the rectangular plot for the second series was somewhat lower than that for the first series, which implies a slowing down of the volatilization rate. No decrease in the temperature of the top 0.08 m soil layer was

Table 2 Rate of volatilization of tri-allate determined with the aerodynamic (AD), Bowen-ratio (BR), theoretical profile (TP) and Box (B) methods after application at the Vredepeel field in 1993. Day 0 = day of application (April 6). The application ended at 14.50 h

Day	Starting time air sampling	Flux density (% of dosage h^{-1})			
	(h)	AD	BR	TP	B
0	15.56	2.8	2.0	2.3	1.1
0	17.32	2.4	1.3	1.5	0.67
1	14.30	0.40	0.34	0.24	0.14
1	15.45	0.35	0.22	0.21	0.15
2	15.52	0.39	0.26	0.18	0.15
2	17.12	0.30	0.19	0.16	0.13
7	12.32	0.043[a]	0.043[a]	0.07	0.06
7	14.56	0.016[a]	0.010[a]	0.04	0.05
14	11.26	0.12	0.16	0.12	0.03
14	15.27	0.018[a]	0.020[a]	0.03	0.03

[a] extract concentrated for analysis.

measured (See Annex 1, Table 1). However, it takes some time before a decrease in net radiation results in a decrease in soil temperature at a depth of 0.08 m. Therefore, the temperature at the soil surface could well have decreased already during the second series, thereby contributing to a decrease in the rate of volatilization.

At about 1.0 d after application, the hourly volatilization rates determined were on average 0.15 times those determined on the day of application. This cannot be explained by a similar decrease in the areic mass of tri-allate remaining in the top layer of the soil profile, because tri-allate in soil decreased comparatively slowly (See Figure 6). In the evening on the day of application and in the subsequent night, 4.5 mm of rain fell. Rain water penetrating the soil will have resulted in some downward transport of a fraction of the pesticide dosage away from the soil surface. This downward transport can be expected to reduce the rate of volatilization of pesticide from the soil surface. Further, the low net radiation (about 110 W m^{-2}) and air temperature (about 8.4 °C as measured at 0.3 m) prevailing in the afternoon of the first day after the day of application compared with the net radiation and air temperature in the afternoon of the day of application (about 170 W m^{-2} and 9.7 °C, respectively; See Figure 4C) can be expected to have contributed to the decrease in volatilization rate.

During the afternoon of the second day after the day of application, the hourly rates of volatilization determined for the first measuring period were not much different from those determined for the preceding afternoon: for the agrometeorological methods it was on average 0.28% of the dosage and for the Box method it was 0.15% of the dosage. Again, the volatilization rate for the second measuring period (late afternoon) was somewhat lower than that for the first measuring period. The decrease in the rate of volatilization could be explained by the cooling down of the soil surface, as caused by a substantial decrease in net radiation: from 146 to 86 W m^{-2} (see Annex 1, Table 2).

At 6.9 d after application, the rate of volatilization of tri-allate was substantially lower than that determined at about 2 d after its application. The average rate of volatilization as determined with the agrometeorological methods was 0.05% of the dosage per hour (s.d. = 0.02%). The rate of volatilization determined with the Box method was slightly higher: 0.06% of the dosage. About 2.5 h later, volatilization rates were lower. The volatilization rate determined with the agrometeorological methods for the second period was about 0.3 times that for the first period. With the Box method, the rate of volatilization in the second period was only slightly lower (about 0.8 times) than that in the first period on this day.

At 13.9 d after application (around noon), the average rate of volatilization of tri-allate as determined with the agrometeorological methods was substantially higher than that determined at 7 d after application. The average hourly volatilization rate as determined with the agrometeorological methods was 0.13% (s.d. = 0.02). On this day, the net radiation reached higher levels as compared with that measured a week earlier (See Figure 4C). A higher net radiation results in a higher temperature at the soil surface, thereby increasing the rate of volatilization of the pesticide. The hourly rate of volatilization as determined with the Box method (0.03% of the dosage) was lower than that determined with the agrometeorological methods. This rate is about half that determined with the Box method at 7 d after application. In the afternoon, the average rate of volatilization as determined with the agrometeorological methods was about 0.15 times that determined around noon. This decrease can be explained by the drying out of the soil surface, because at low soil moisture contents (below a few percent), adsorption of pesticides onto soil particles becomes stronger. In the afternoon, the moisture content in the top 5 mm was measured to be about 5%, so the soil moisture content in the upper part of this layer may have been in the range which results in increased adsorption of the pesticides. For the Box method, no corresponding decrease in the volatilization rate was found.

As the first measurement of the rate of volatilization of tri-allate started one hour after its application, the volatilization rate of tri-allate during the first hour can be expected to have been higher than that determined for the first series (i.e. the second hour after application).

At 14 d after application, the rate of volatilization determined in the morning was still about 0.4 times that determined on the first day after the day of application. This indicates that a substantial mass of pesticides still remained on the soil surface (See Section 3.2).

The volatilization rate determined with the agrometeorological methods was mostly substantially higher than that determined with the Box method. The differences in volatilization rate as determined with the four methods used in this study are discussed in more detail in Section 3.5.

3.4.2 Rate of volatilization of ethoprophos

The rates of volatilization of ethoprophos from the soil, as obtained with the AD, BR, TP and Box methods for 10 or 11 times after the application are given in Table 3. For the first hour after application, the hourly rate of volatilization amounted to 3.4% of the dosage for both the AD and the BR-method. During the following 5 hours, the volatilization rate of ethoprophos decreased substantially. At 6 hours after application, the average volatilization rate as determined with the agrometeorological methods was 0.79% of the dosage (n = 3, s.d. = 0.28). The volatilization rates as determined with the Box method on the day of application were about 0.25 times the average rate for the agrometeorological methods.

The decrease in the volatilization rate of ethoprophos towards the evening can be related to the decrease in the net radiation (See Figure 4C). A lower net radiation results in less energy available for the volatilization of pesticide at the soil surface.

At 1.1 d after the application, the hourly rate of volatilization of ethoprophos as determined with the agrometeorological methods had decreased to 0.13% of the dosage (n = 3, s.d. = 0.03). About one hour later, the volatilization rate as determined with these methods was somewhat lower: 0.11 % (s.d. = 0.03). On this day, the rate

Table 3 Rate of volatilization of ethoprophos determined with the aerodynamic (AD), Bowen-ratio (BR), theoretical profile (TP) and Box (B) methods after its application at the Vredepeel field in 1993. Day 0 = day of application (April 6). The application ended at 12.40 h

Day	Starting time air sampling	Flux density (% of dosage h^{-1})			
	(h)	AD	BR	TP	B
0	12.42	3.4	3.4	-	-
0	15.56	1.2	0.84	0.94[a]	0.26
0	17.32	1.1	0.57	0.69[a]	0.18
1	14.30	0.15	0.13	0.10[a]	0.04
1	15.45	0.15	0.10	0.10[a]	0.04
2	15.52	0.29	0.20	0.12[a]	0.06
2	17.12	0.22	0.14	0.11[a]	0.06
7	12.32	0.013[a]	0.013[a]	0.04[a]	0.022
7	14.56	0.003[a]	0.002[a]	0.02[a]	0.016
14	11.26	0.11	0.16	0.09[a]	0.016
14	15.27	0.007[a]	0.007[a]	0.01[a]	0.010

[a] extracts concentrated for analysis.

of volatilization as determined with the Box method was lower than that determined with the agrometeorological methods (0.3 times).

In the afternoon of the first day after the day of application, the average hourly volatilization rate as determined with the methods was about 0.15 times that determined in roughly the same period on the day of application. This cannot be explained by a similar decrease in the areic mass of pesticide remaining in the top layer of the soil profile, as there was hardly any decrease in the fraction of ethoprophos remaining in the topsoil (See Figure 5). However, due to rainfall during the preceding night, a fraction of the ethoprophos applied may have been transported downwards, thereby decreasing the fraction available for volatilization. Presumably, the lower net radiation and air temperature prevailing in the afternoon of the first day after the day of application, as compared with those for the afternoon of the day of application (See Figure 4C), have contributed to the decrease in the volatilization rate.

At 2.1 d after application, the rate of volatilization as determined with each agrometeorological method was higher than the rates determined with these methods on the preceding afternoon. The average hourly rate of volatilization was 0.20% of the dosage (s.d. = 0.09). About 1.3 hours later, the volatilization rate had decreased somewhat, which can be explained by the cooling down of the soil surface (see Annex 1, Table 2). Again, the volatilization rate as determined with the Box method was lower than that determined with the other methods. For the Box method, no decrease in the volatilization rate was measured in the course of the afternoon. The higher volatilization rates determined on this day compared with those determined on the day before can be explained by the higher air temperatures during the measurement periods on the second day after the day of application compared with those during the measurement periods of the day before: 9.8 vs. 8.3 °C (both at 0.3 m).

At 7.0 d after application, the rate of volatilization of ethoprophos as determined with the agrometeorological methods was on average about 0.1 times that determined with these methods at 2.1 d after application. In the course of the afternoon, the rate of volatilization decreased to about 0.3 times that in the first period. This decrease could be caused by an increased adsorption of ethoprophos onto soil particles as a result of the drying out of the soil surface. The volatilization rates determined with the Box method showed a comparatively small decrease in the course of the afternoon.

At 14.0 d after the application, the hourly rate of volatilization of ethoprophos as determined with the agrometeorological methods was higher than the rate determined with these methods at 7.0 d after application: on average 0.12% of the dosage (s.d. = 0.04). In the afternoon of this day, volatilization as determined with the agrometeorological methods decreased substantially: on average it was 0.007% of the dosage (s.d. = 0.001). Similar to the decrease in volatilization rate during the afternoon of the 7th day after the day of application, this decrease could be due to increased adsorption of the pesticide as a result of drying out of the uppermost soil layer. The decrease in the volatilization rate during the afternoon as determined with the Box method was small compared with that determined with the agrometeorological methods.

3.4.3 Rate of volatilization of parathion

The rates of volatilization of parathion from the soil, as obtained with the AD, BR, TP and B methods at 10 or 12 times after the application, are given in Table 4. The highest volatilization rates, as determined with the AD and BR methods, were obtained for the first two hours after application: on average 0.25% of the dosage per hour. During the next 4 hours, the hourly volatilization rate decreased to about 0.12% of the dosage. The average volatilization rate at the end of the afternoon tended to be somewhat higher (0.16%) than that determined with the AD and BR methods about 1.5 h earlier, despite the lower net radiation. This may have been due to moistening of the soil surface, as some rain fell (about 1 mm) between the third and fourth air sampling series.

At 1.2 d after application, the rate of volatilization of parathion as determined with the AD and BR methods was about 0.11 times that determined during the first few hours after application: about 0.03% of the dosage per hour. The volatilization rate as determined with the Box method was about 0.25 times the average rate determined with the other methods. The volatilization rate during the second measuring period of the afternoon was on average slightly higher than that during the first measuring period. Presumably, the lower net radiation and the lower air temperature during the measurements on the first day after the day of application, compared with those during the measurements on the day of application, contributed to the decrease in volatilization rate.

At 2.2 d after application, the hourly rate of volatilization of parathion as determined with the agrometeorological methods was 0.027% of the dosage (n = 3, s.d. = 0.012). Late afternoon, the average hourly volatilization rate as determined with these methods was somewhat lower: 0.022% of the dosage (s.d. = 0.008). This decrease

Table 4 Rate of volatilization of parathion determined with the aerodynamic (AD), Bowen-ratio (BR), theoretical profile (TP) and Box (B) methods after application at the Vredepeel field in 1993. Day 0 = day of application (April 6). The application ended at 11.00 h

Day	Starting time air sampling	Flux density (% of dosage h^{-1})			
	(h)	AD	BR	TP	B
0	11.03	0.29	0.19	-	-
0	12.42	0.25	0.24	-	-
0	15.56	0.14	0.10	0.10[a]	0.023
0	17.32	0.20	0.11	0.07[a]	0.015
1	14.30	0.03	0.027	0.017[a]	0.006
1	15.45	0.04	0.026	0.019[a]	0.008
2	15.52	0.04	0.026	0.016[a]	0.008
2	17.12	0.03	0.020	0.015[a]	0.008
7	12.32	0.006[a]	0.006[a]	0.007[a]	0.004
7	14.56	0.002[a]	0.001[a]	0.002[a]	0.005
14	11.26	0.035	0.049	0.018[a]	0.004
14	15.27	0.002[a]	0.002[a]	< 0.003[a]	0.003

[a] extracts concentrated for analysis.

in the rate of volatilization can be explained by the cooling down of the soil surface (see Annex 1, Table 2). Again, lower rates of volatilization were determined with the Box method. With this method, no decrease was determined in the volatilization rate during the afternoon.

At 7.1 d after application, the rate of volatilization was substantially lower than that measured at 2.2 d after application. For the agrometeorological methods, the rate was about 0.25 times that determined at about 2.2 d after application, whereas for the Box method the volatilization rate was about 0.5 times that determined 5 d earlier. Later in the afternoon, the volatilization rate as determined with the agrometeorological methods was on average 0.3 times that determined earlier on the day, which is possibly due to the increased adsorption of parathion onto the soil as the soil surface dries out. No corresponding decrease was measured with the Box method.

At 14.1 d after application, the hourly volatilization rate as determined with the agrometeorological methods was on average six times that determined with these methods at 7.1 d after application: 0.034% of the dosage (n = 3, s.d. = 0.016). No corresponding increase was measured with the Box method. During the second half of the afternoon, the average volatilization rate as determined with the AD and BR methods was substantially lower than that determined around noon: the average rate for these two methods was 0.002% of the dosage. Again, this decrease is possibly related to the increased adsorption of parathion at low soil moisture contents. For the first measuring period, the volatilization rate as measured with the Box method was about 0.12 times that determined with the other methods, but for the second period it was 1.5 times as high.

3.5 Comparison of methods

For each pesticide, the average ratio between the volatilization rates as obtained for each pair of methods and its significance is given in Table 5. For the comparison of an agrometeorological method with the Box method, the measurements of the second series in the afternoon of the 7th and the 14th day after application were not taken into account. During those afternoons, the rate of volatilization as determined with the agrometeorological methods decreased strongly, which can be explained by the drying out of the soil surface (See Section 3.4). No corresponding decrease in the volatilization rate was found when using the Box method. Presumably, there were no similar changes in volatilization conditions within the box as those occurring outside the box.

On average, the difference in the rate of volatilization of each pesticide as determined with two agrometeorological methods was comparatively small. The rate of volatilization determined with the aerodynamic method was 1.3 times that determined with the Bowen-ratio method, which is significant at the 95% confidence level (P-values ranging from 0.01 to 0.03). The ratio between the volatilization rates as determined with these two methods is the same for all pesticides, because of the linear relationship used in both methods between the volatilization rate and the concentration gradient. The latter was measured between the same heights for both methods.

The rate of volatilization of parathion as determined with the aerodynamic method was 1.7 times that determined with the theoretical profile method (P-value 0.004). For ethoprophos and tri-allate, there was no significant difference between the volatilization rates determined with these methods.

No significant differences were found between the volatilization rates determined with the Bowen-ratio and the theoretical profile methods, the average ratio being 1.0.

The rates of volatilization of each pesticide as determined with the aerodynamic, the Bowen-ratio and the theoretical profile methods were significantly higher than

Table 5 Comparison of the volatilization rates determined for each pair of methods for ethoprophos, tri-allate and parathion. AD = aerodynamic, BR = Bowen-ratio, TP = theoretical profile, B = Box method

Comparison	Ethoprophos		Tri-allate		Parathion	
	ratio[a]	95% c.i.[b]	ratio[a]	95% c.i.[b]	ratio[a]	95% c.i.[b]
AD vs. BR	1.3 (s)	1.0-1.5	1.3 (s)	1.0-1.6	1.3 (s)	1.1-1.6
AD vs. TP	1.0 (ns)	0.5-1.9	1.1 (ns)	0.8-1.7	1.7 (s)	1.3-2.4
BR vs. TP	0.8 (ns)	0.4-1.5	0.9 (ns)	0.6-1.3	1.3 (ns)	0.9-1.8
AD vs. B	3.6 (s)	1.9-6.8	2.4 (s)	1.5-3.7	5.3 (s)	3.1-9.0
BR vs. B	2.8 (s)	1.4-5.3	1.8 (s)	1.1-2.9	4.1 (s)	2.4-7.0
TP vs. B	2.7 (s)	1.9-3.8	1.7 (s)	1.2-2.5	2.9 (s)	2.0-4.0

[a]s = significant; ns = not significant; [b]95% confidence interval.

those measured with the Box method (P-values ranging from less than 0.001 to 0.02). The average ratio between the volatilization rates as determined with these methods and the Box method were 3.8, 2.9 and 2.4, respectively.

For parathion, the ratio between the volatilization rates as determined for each pair of methods was significantly different from 1.0, except when comparing the Bowen-ratio method with the theoretical profile method. For ethoprophos and tri-allate, the ratio between the volatilization rates determined for each pair of methods was significantly different from 1.0, except when comparing the aerodynamic and Bowen-ratio methods with the theoretical profile method.

It should be noted that the range in values for the ratio when comparing the volatilization rates determined with an agrometeorological method with those determined with the Box method was wide as compared with the range of values when comparing two agrometeorological methods. However, as the average ratio between the volatilization rates as determined with an agrometeorological method and the Box method was comparatively high, this ratio was still significantly different from 1.0. Furthermore, as the rate of volatilization of parathion was mostly low, inaccuracies in its determination may have contributed to the comparatively high ratio between the volatilization rate determined with the agrometeorological methods and that determined with the Box method.

During the afternoon of the 7th and 14th days after the day of application, there was a substantial decrease in the volatilization rates measured (See Section 3.4). On both afternoons, the decrease with time of the rate of volatilization was highest for the BR method. Possibly, this method was the most sensitive to the changes in meteorological and soil conditions during those afternoons.

On the 14th day after the day of application, the rates of change in the hourly net radiation, air temperature and soil heat flux density were higher than those measured on previous days (See Section 3.1). Possibly, the similar volatilization rates as determined on that day with the Box method are due to an effective shielding of the soil surface by the box to changes in meteorological conditions outside the box. With the other methods, there was a great difference in volatilization rate determined in the course of the afternoon.

The sprayed surface area for which the volatilization rate was determined using the Box method is small compared to that for the AD and BR methods. As the Box was regularly replaced to a new undisturbed site, variations in the volatilization rate can be expected as a result of local differences in the areic mass of pesticide remaining on the soil surface and those in the moisture and organic matter contents of the soil surface layer. However, the change in the volatilization rate after moving the Box to another site was rather small. On the first and second days after the day of application, when changes in weather conditions during the measurement periods were comparatively small, the change in volatilization rate after moving the Box a few metres away to another site was comparatively small, i.e. less than 25%. However, more extensive, simultaneous measurements are needed to assess the extent of the variation in the emission flux density within the whole sprayed area.

3.6 Comparison of the pesticides

For each method, the average ratio between the volatilization rates for each pair of pesticides is given in Table 6. The ratio for each pair of pesticides was significantly different from 1.0 for all methods. The average volatilization rate of tri-allate was about 2.3 times that of ethoprophos and about 12 times that of parathion. The average volatilization rate of ethoprophos was about 6 times that of parathion.

The course with time of the average hourly rate of volatilization of tri-allate, ethoprophos and parathion as determined with the agrometeorological methods is presented in Figure 8. Following a rather sharp decrease in the volatilization rate during the first 24 hours, a more gradual decline in the volatilization rate was determined. On the first and second days after the day of application, there were no great differences between the rates of volatilization as determined during the afternoon. However, on the 7th and the 14th day after application, the decrease in the volatilization rate of each pesticide in the course of the afternoon was substantial. Presumably, the decrease in the volatilization rate on these days is largely due to the drying out of the soil surface layer.

During the first 24 h after application, the ratio between the volatilization rate of tri-allate and that of parathion as determined with the agrometeorological methods decreased from about 22 to 10 and that between the volatilization rate of ethoprophos and parathion decreased from about 9 to 5. As no measurement was done on the volatilization rate of tri-allate during the first hour after application, the decrease in the ratio during the first 24 h was probably greater than that measured. Thereafter, the ratios remained mostly at the same level. For the ratio between the volatilization rate of tri-allate and ethoprophos, there was no distinct decrease during the first 24 h after application. Throughout the first two weeks after application, the values for this ratio ranged from 1.4 to 2.8.

Table 6 Comparison of volatilization rates as determined for each pair of pesticides with the aerodynamic, Bowen-ratio, theoretical profile and Box methods

Comparison	Aerodynamic		Bowen-ratio		Theoretical profile		Box	
	ratio	c.i.[a]	ratio	c.i.[a]	ratio	c.i.[a]	ratio	c.i.[a]
Tri-allate vs. ethoprophos	2.2	1.6-3.1	2.2	1.6-3.1	2.0	1.6-2.4	2.9	2.4-3.5
Ethoprophos vs. parathion	4.6	3.0-7.2	4.8	3.2-7.2	7.0	5.7-8.7	6.1	4.4-8.6
Tri-allate vs. parathion	9.2	6.7-13	9.5	6.8-13	13	9.6-18	18	12-28

[a] 95% confidence interval.

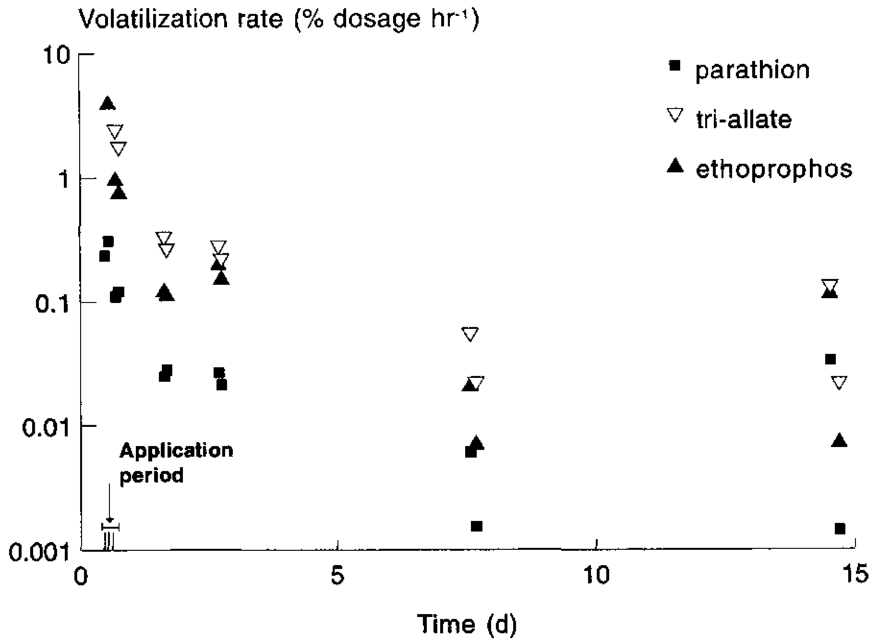

Fig. 8 Average hourly rates of volatilization of tri-allate, ethoprophos and parathion from soil as determined with the agrometeorological methods after their application at the Vredepeel field in 1993. Zero time = April 6, 0.00 h. The applications of parathion, ethoprophos and tri-allate (indicated by bars) ended at 11.00, 12.40 and 14.50 h, respectively

The ratio between the volatilization rate of tri-allate and that of parathion (Table 6) was higher when using the Box method (18) than when using the AD and BR methods (9). The average ratio between the volatilization rate determined with an agrometeorological method and that determined with the Box method was significantly different from 1.0 (See Section 3.5). Presumably, volatilization conditions (e.g. soil moisture content and temperature near the soil surface) within the box have been different from those outside the box. This can result in the ratio between the volatilization rates for a pair of pesticides as determined with the Box method to be different from the ratio determined with an agrometeorological method.

It should be noted that as the pesticides were not applied simultaneously, a full comparison between the hourly percentages of the dosage of each pesticide lost by volatilization at comparatively short times after application is not possible. However, in the course of time the differences between the times elapsed after the application of each pesticide became negligible.

The rate of volatilization of a pesticide can be related to its vapour pressure. As an example, the volatilization rates of ethoprophos, tri-allate and parathion as determined by the AD, BR and TP methods at about one day after application are plotted against their vapour pressure at 25 °C in Figure 9A. There is no simple relationship between the volatilization rate and the vapour pressure, so other physico-chemical properties of the pesticide need to be taken into account, e.g. the coefficient for the adsorption onto soil components. In Figure 9B, the volatilization rates of ethoprophos, tri-allate and parathion are plotted against the percentage of the pesticide in the gas phase of the soil system. There appears to be a much better relationship between the volatilization rate of a pesticide and its fraction in the gas phase of the soil system than between its volatilization rate and vapour pressure.

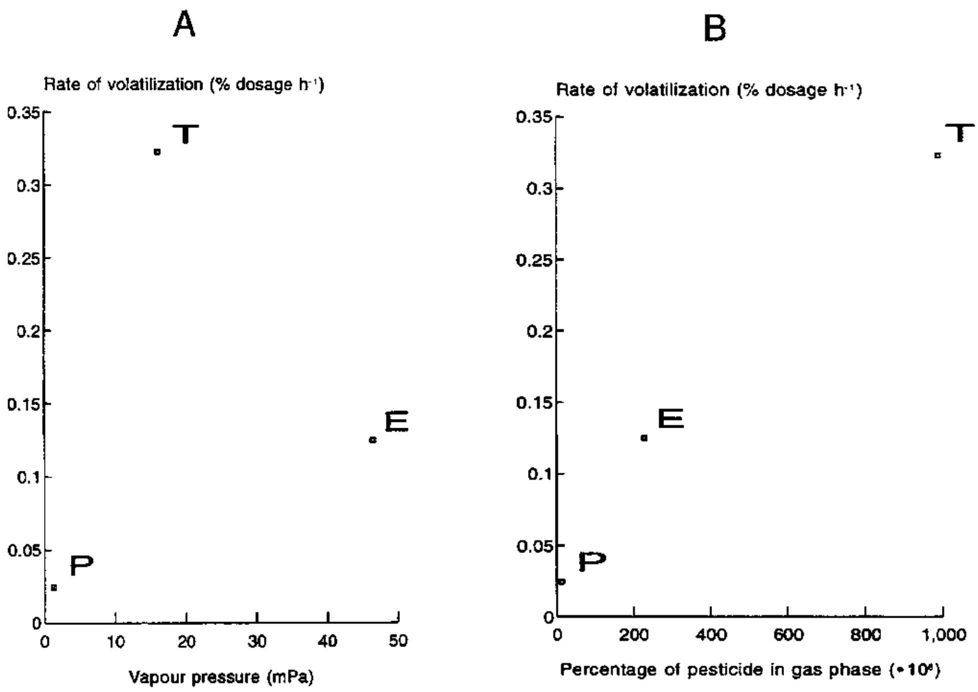

Fig. 9. Rate of volatilization of tri-allate (T), ethoprophos (E) and parathion (P) as determined by the AD, BR and TP methods at about one day after application versus their vapour pressures at 25 °C (A) and versus their percentages in the gas phase of the soil system (B).

4 Discussion and conclusions

The highest rates of volatilization of tri-allate were determined during the first few hours after application. During the second hour after application, the average hourly volatilization as determined with the AD, BR and TP methods was 2.4% of the dosage. No measurements were made during the first hour after application; presumably the rate of volatilization was higher than that determined during the second hour after application. On the first and second days after the day of application, the hourly volatilization rates of tri-allate determined with the agrometeorological methods amounted to a few tenths of percent of the dosage. Thereafter, the hourly volatilization rates decreased further to a few hundredths of percent of the dosage. Even at 14 d after the day of application, hourly volatilization rates of about 0.1% of the dosage were determined around noon, which is not much different from the hourly rates as determined during the first two days after the day of application.

The course with time of the rate of volatilization of ethoprophos was similar to that of tri-allate. The highest hourly rate of volatilization determined with the three agrometeorological methods was determined during the first hour after application, i.e. 3.4% of the dosage. On the first and second days after the day of application, the hourly rate of volatilization of ethoprophos ranged from 0.1 to 0.2% of the dosage. Thereafter, the hourly volatilization rate decreased further to around 0.01% of the dosage. Around noon on the 14th day after the day of application, the hourly volatilization rate had increased to 0.1% of the dosage.

The highest hourly rate of parathion volatilization occurred shortly after application, i.e. 0.25% of the dosage. During the first 7.5 h after the application, the hourly rate of volatilization determined with the three agrometeorological methods decreased to about 0.1% of the dosage. On the first and second days, hourly volatilization rates were substantially lower, ranging from 0.02 to 0.03% of the dosage, as determined with the agrometeorological methods. On the 7th and 14th days after the day of application, hourly volatilization rates had mostly decreased to below one hundredth percent of the dosage.

Because the rate of volatilization of pesticide decreases with time, larger sampling volumes are needed at longer times after application. In this study, 2-h instead of 1-h air samples were taken to enable lower volatilization rates to be quantified. However, longer air sampling periods may mask changes in volatilization rate resulting from changes in meteorological and soil conditions within the sampling period. For example, the rate of volatilization of pesticides is low under dry topsoil conditions, but upon wetting of the soil surface a substantial increase in the volatilization rate can occur within a short time. Further lowering of the limit of detection of pesticides in air is needed to measure the effect of changing conditions.

The percentages of the dosage of tri-allate, ethoprophos and parathion lost by volatilization during the first two weeks after application can be estimated from the average daily volatilization rates. It is assumed that volatilization during night-time is negligible. If no measured values were available for a day, the average daily volatilization rate was obtained by averaging the volatilization rates determined on the nearest day of measurement before and after that day. As expected, the greatest loss by volatilization was calculated for tri-allate, i.e. about 29% of its dosage. For ethoprophos, the percentage of its dosage calculated to be lost by volatilization was about 24%. The loss of parathion by volatilization during the first two weeks after application of about 4% of its dosage was much lower than that for the other two pesticides. At two weeks after application, substantial fractions of the pesticides remained in the soil, ranging from 30 to 50% of the dosage, so continued loss by volatilization can be expected.

The ratio of 2.3 (Table 6) between the average volatilization rate of tri-allate and that of ethoprophos does not correspond to the ratio of 0.3 between their vapour pressures at 25 °C (See Section 1, Table 1). Therefore, other factors need to be taken into account to explain the difference in volatilization rate determined, e.g. the partitioning of the pesticide between the liquid and gas phases and that between the liquid and solid phases. Assuming the volatilization rate of a pesticide to be related to its concentration in the gas phase of the uppermost soil layer, an estimate can be made for the ratio between the volatilization rates of tri-allate and ethoprophos for the Vredepeel soil. Using the percentage of organic matter and the volume fractions of the liquid and solid phases measured in that soil together with the data on the Henry and adsorption coefficients as presented in Table 1, the ratio between the concentrations in the gas phase at 25 °C is calculated to be 3.8. Assuming this ratio to be the same as that at the temperatures prevailing in the field, it corresponds reasonably with the average ratio between the volatilization rates measured.

During the first 24 h after the application of tri-allate, the ratio between the rate of volatilization of tri-allate and that of parathion, as determined with the agrometeorological methods, decreased from about 22 to 10. Thereafter, the ratio between the volatilization rates remained roughly the same (about 9). Shortly after application the pesticides are present in a thin film sprayed on the soil surface, so the ratio between the initial volatilization rates could be related to that between their Henry coefficients. Later on, most of the pesticide will be adsorbed to the soil components. Then, the ratio between the volatilization rates more likely corresponds to the ratio between the concentrations of each pesticide in the gas phase of the uppermost soil layer. However, the ratio between the Henry coefficients of tri-allate and parathion (75, See Table 1) is lower than the ratio between their concentrations in the gas phase (102). Higher values for the vapour pressure of parathion have been reported in the literature. For example, RIVM (1990) reported a vapour pressure of 5 mPa at 20 °C, which would result in a ratio between the concentrations in the gas phase of 27, which is much closer to the ratio between the volatilization rates measured.

For ethoprophos and parathion, the initial ratio between their volatilization rates as determined with the agrometeorological methods (up to 9) does not correspond to the ratio between their Henry coefficients (0.9, see Table 1). The slightly lower Henry coefficient of ethoprophos would indicate it to be less volatile than parathion, but the measurements in the field showed the contrary. As parathion was applied earlier than ethoprophos, a higher ratio between the initial rates of volatilization of ethoprophos and parathion measured at the same time can be expected than when these pesticides had been applied simultaneously. The ratio between the volatilization rates of ethoprophos and parathion as estimated from the concentrations of these chemicals in the gas phase of the soil near the surface is about 27, which indicates ethoprophos to be the more volatile compound. This is higher than the average ratio between their volatilization rates of about 5 obtained from the measurements following the first 24 h. Again, the vapour pressure of parathion may be higher than that used in the calculations. For example, using a vapour pressure of 5 mPa at 20 °C (RIVM, 1990), the ratio between the concentrations in the gas phase is calculated to be about 7, which is not much higher than the average ratio between the volatilization rates measured.

When discussing differences in the course with time of the rate of volatilization of pesticides, accurate data on their physico-chemical characteristics, such as vapour pressure and water solubility, are needed. However, the quality of the data on these characteristics published in the literature may be poor and sometimes different data for a particular characteristic are reported. Adequate information is needed on the methods of measurement and their accuracy when using such data on the physico-chemical characteristics of pesticides for predictions on their behaviour. As vapour pressures and water solubilities of most pesticides are rather low, high standards need to be met to measure these characteristics accurately.

Majewski et al. (1993) measured the rate of volatilization of tri-allate with the AD method during the first 5 d after its spraying onto a moist clayey soil at about 18 °C. High rates of volatilization were measured directly after application. At first, the rate of volatilization decreased rather sharply, but thereafter the decrease was more gradual. During the first 3 hours, about 8% of the dosage was lost by volatilization. From the present study, the loss of tri-allate by volatilization during the first 3 hours can be estimated from the volatilization rates determined for the 2nd and 3rd hours after application and the estimated rate for the 1st hour obtained by linear backward-extrapolation. The volatilization loss is estimated to be about 8%, which is similar to the loss determined by Majewski et al. (1993), although the ambient temperatures of around 10 °C shortly after application at the Vredepeel field were comparitively low. Presumably, other factors compensated for this effect. For example, the adsorption of tri-allate onto the sandy soil in this study may have been less strong than that on the clayey soil in the study of Majewski et al. (1993).

At 14 d after application, substantial fractions of each dosage were still present in the top 0.03 m layer. Therefore, volatilization can be expected to continue for a prolonged period. When the top few mm of the soil layer remain moist or become rewetted, comparatively high rates of volatilization can be expected, in the order of a few tenths of percent of the dosage for ethoprophos and tri-allate and a few hundredths of percent of the dosage for parathion. However, when the top soil dries out, volatilization rates can be expected to reduce strongly. This is also illustrated by the field experiment by Majewski et al. (1993), who measured a 16-fold increase in the rate of volatilization of tri-allate from a clayey soil after heavy rainfall on a comparatively dry soil surface.

For all three pesticides in this study, the rate of volatilization as determined with the AD method was 1.3 times that determined with the BR method and this difference was significant. Majewski et al. (1990) measured the rate of volatilization of nitrapyrin, lindane, diazinon and chlorpyrifos from a bare soil with the AD and BR methods at nine times during the first two days after application. The rate as determined with the AD method was not significantly different from that determined with the BR method. However, the average ratio between the rates measured with these methods was about 1.2 (95% confidence interval 0.7 - 2.0), which is not much different from the ratio determined in the present study. Possibly, significance of a difference depends on the type and range in weather and soil conditions at the times of measurement.

The differences in volatilization rates as determined with the AD and TP methods were not significant (except for parathion); the average ratios for ethoprophos and tri-allate ranged from 1.0 to 1.1 and the ratio for parathion was 1.7. Majewski et al. (1990) measured the rate of volatilization of nitrapyrin, lindane, diazinon and chlorpyrifos from a bare soil with the AD and TP methods at ten times during the first three days after application. There was no significant difference in the volatilization rate as measured with these methods, the average ratio between the volatilization rates ranging from 0.8 to 1.0. Majewski et al. (1991) measured the rate of volatilization of chlorthal from soil with the AD and TP methods at 19 times during the first 21 d after the day of application. At four times, the shape of the vertical concentration profile in air did not seem logical. Therefore, only the data collected at the other times are used for the comparison. The average volatilization rate determined with the AD method was 0.7 (95% confidence interval 0.5 - 0.9) times that determined with the TP method. Presumably, measurements with the AD method under-estimated the volatilization rate because of the comparatively small upwind fetch (50 m) compared with the measurement height (0.8 m).

In our study, the differences in volatilization rates as determined with the BR and TP methods were not significant; the average ratio ranged from 0.8 to 1.3. Majewski et al. (1990) also found no significant differences when comparing the BR and TP methods for the determination of the rate of volatilization of four pesticides from bare soil at six times during the first three days after application (average ratios ranging from 1.0 to 1.1).

The rates of volatilization of the pesticides as determined with the Box method were on average 0.3 times those determined with the agrometeorological methods (excluding the rates of volatilization from a comparatively dry soil surface, See Section 3.5). Although the range of values of the ratio between the volatilization rate determined with the Box method and that determined with an agrometeorological method was comparatively wide, the differences were significant. The comparatively small range in volatilization rates as determined with the Box method indicates that the covering of the soil surface with the box attenuated the differences in weather conditions and thereby reduced the changes in the rate of volatilization. To quantify this, data are needed on the course with time of the factors affecting volatilization within the box and outside the box, such as the moisture content and the temperature at the soil surface. Such data could also be useful for the further development of this method, while keeping its advantages (low-cost equipment and easy to handle).

In the present study, all air samples were taken under unstable atmospheric conditions as indicated by the negative values for the Richardson number. Therefore, the comparison between the methods to determine the rate of volatilization from soil is not complete. Majewski et al. (1990) compared the volatilization rates determined with five methods, but all measurements were done under unstable atmospheric conditions too. Majewski et al. (1991) compared the TP with the AD method for the determination of the volatilization of chlorthal from soil. In their experiment, the ratio between the volatilization rate as determined with the TP and the AD methods under stable conditions was 1.9 (95% confidence interval 0.8 - 4.7), whereas under unstable conditions it was somewhat lower, i.e. 1.4 (95% confidence interval 1.1 - 1.6). Probably, the upwind fetch was insufficient for the AD method and this may have contributed to the difference. More measurements under a wider range of weather conditions are needed to compare the methods and to assess whether differences between methods are significant.

The highest 1-h concentrations of tri-allate, ethoprophos and parathion in air were measured at the downwind edge of the rectangular plot shortly after their application. The concentrations at 1.5 m above the ground ranged up to 5.3, 2.9 and 0.6 $\mu g\ m^{-3}$, respectively. During the first two days after application, the concentrations in air were measured to be about 0.7, 0.5 and 0.1 $\mu g\ m^{-3}$, respectively. On the 7th and 14th days, the concentrations of tri-allate and ethoprophos ranged from a few hundredths to a few tenths $\mu g\ m^{-3}$. On those days, the concentrations of parathion in air remained below 0.1 $\mu g\ m^{-3}$. The maximum acceptable concentration (MAC) of parathion in air for occupational exposure (40 h per week, 8 h per day) is 100 $\mu g\ m^{-3}$ (Labour Inspection, 1992). As the concentrations of parathion measured in air were a factor 100 or more lower, the risk for the health of people living in the vicinity of the application seems to be comparatively small. For ethoprophos and tri-allate, no MAC-values have been adopted yet.

In the present study, tri-allate and ethoprophos were sprayed onto the surface. Usually, these compounds are incorporated into the soil directly after application, which will reduce the rate of volatilization substantially and result in lower concentrations in air.

References

Dörfler, U., Adler-Köhler, R., Schneider, P., Scheunert, I. and F. Korte, 1991. 'A laboratory model system for determining the volatility of pesticides from soil and plant surfaces'. *Chemosphere*, 23: 485-496.

Jury, W.A., W.F. Spencer & W.J. Farmer, 1983. 'Use of models for assessing relative volatility, mobility, and persistence of pesticides and other trace organics in soil systems'. In: *Hazard assessment of chemicals: current developments*, J. Saxena (Ed.), vol 2, 1-43, Academic Press, New York.

Labour Inspection, 1992. 'De nationale MAC-lijst 1992 (The national MAC-list 1992)'. *Publicatie P 142*. Ministry of Social Affairs and Employment, Department of Labour, Voorburg, The Netherlands.

Majewski, M.S., R. Desjardins, P. Rochette, E. Pattey, J. Seiber & D.E. Glotfelty, 1993. 'Field comparison of an eddy accumulation and an aerodynamic-gradient system for measuring pesticide volatilization fluxes'. *Environmental Science and Technology*, 27: 121-128.

Majewski, M.S., D.E. Glotfelty, K.T. Paw U & J.N. Seiber, 1990. 'A field comparison of several methods for measuring pesticide evaporation rates from soil'. *Environmental Science and Technology*, 24: 1490-1497.

Majewski, M.S., D.E. Glotfelty & J.N. Seiber, 1989. 'A comparison of the aerodynamic and the theoretical-profile shape methods for measuring pesticide evaporation from soil'. *Atmospheric Environment*, 23: 929-938.

Majewski, M.S., M.M. McChesney & J.N. Seiber, 1991. 'A field comparison of two methods for measuring DCPA soil evaporation rates'. *Environmental Toxicology and Chemistry*, 10: 301-311.

Parmele, L.H., Lemon, E.R. and A.W. Taylor, 1972. 'Micrometeorological measurement of pesticide vapor flux from bare soil and corn under field conditions'. *Water, Air and Soil Pollution*, 1: 433-451.

Pruitt, W.O., D.L. Morgan & F.J. Lourance, 1973. 'Momentum and mass transfers in the surface boundary-layer'. *Quarterly Journal of the Royal Meteorological Society*, 99, 370-386.

Spencer, W.F. & M.M. Claith, 1974. 'Factors affecting vapor loss of trifluralin from soil'. *Journal of Agriculture and Food Chemistry*, 22: 987-991.

Tomlin, C., 1994. *The Pesticide Manual (10th ed.)*. British Crop Protection Council, Bracknell, Berkshire, UK.

Whang, J.M., C.J. Schomburg, D.E. Glotfelty and A.W. Taylor, 1993. 'Volatilization of fonofos, chlorpyrifos, and atrazine from conventional and no-till surface soils in the field'. *Journal of Environmental Quality*, 22: 173-180.

Wieringa, J. and P.J. Rijkoort, 1983. '*Windklimaat van Nederland (Wind climate of the Netherlands)*'. Staatsuitgeverij, The Hague, The Netherlands.

Wilson, J.D., 1982. 'Estimation of the rate of gaseous mass transfer from a surface source plot to the atmosphere'. *Atmospheric Environment*, 16: 1861-1867.

Unpublished sources

National Institute of Public Health and Environmental Protection (RIVM), 1989. *Milieufiche Ethoprophos.*

National Institute of Public Health and Environmental Protection (RIVM), 1990. *Milieufiche Parathion.*

National Institute of Public Health and Environmental Protection (RIVM), 1991. *Milieufiche Triallate.*

Annex 1 Meteorological data for the calculation of the pesticide volatilization rates

Table 1 Input data for the Bowen-ratio method. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Soil heat flux at 0.08 m depth (W m^{-2})	Δ(soil temperature) (K)	Δ(air temperature) (K)	Δ(vapour pressure) (kPa)	Bowen-ratio coefficient (-)
0	11.00	13.7	0.131	0.138	0.016	0.593
0	12.40	22.9	0.335	0.282	0.024	0.766
0	16.00	27.4	0.047	0.186	0.027	0.461
0	17.30	15.2	-0.180	0.044	0.021	0.133
1	14.30	13.4	0.144	0.236	0.024	0.639
1	15.40	19.2	0.144	0.305	0.027	0.755
2	15.50	32.6	0.017	0.430	0.046	0.621
2	17.10	26.3	-0.195	0.258	0.043	0.399
7	12.30	45.3	0.366	0.458	0.012	1.282
7	15.00	60.3	0.166	0.493	0.026	1.404
14	11.30	77.2	0.577	0.407	0.057	0.444
14	15.30	101.4	0.141	0.412	0.043	0.652

Table 2 Energy balance and the dispersion coefficient of sensible heat. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Net radiation (W m^{-2})	Soil heat flux at the soil surface (W m^{-2})	Sensible heat flux (W m^{-2})	Latent heat flux (W m^{-2})	Dispersion coefficient for sensible heat (m^2 h^{-1})
0	11.00	85	26.5	21.6	36.5	233
0	12.40	202	55.8	63.5	82.9	334
0	16.00	130	32.0	31.1	67.4	248
0	17.30	47	-2.4	5.8	43.6	197
1	14.30	112	27.6	33.1	51.7	208
1	15.40	105	33.3	30.8	40.8	150
2	15.50	146	34.3	42.6	68.6	147
2	17.10	86	7.2	22.5	56.4	130
7	12.30	204	81.2	69.0	53.8	224
7	15.00	164	76.6	51.1	36.4	154
14	11.30	473	133.8	104.1	234.6	380
14	15.30	306	115.2	75.3	115.4	271

Table 3 Data on the Richardson number and the correction factors as used for the aerodynamic method. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Richardson number (-)	Correction factor momentum (-)	Correction factor pesticide (-)
0	11.00	-0.003	0.985	0.863
0	12.40	-0.007	0.966	0.836
0	16.00	-0.004	0.979	0.855
0	17.30	-0.001	0.996	0.879
1	14.30	-0.013	0.940	0.802
1	15.40	-0.023	0.902	0.753
2	15.50	-0.110	0.713	0.541
2	17.10	-0.031	0.873	0.717
7	12.30	-0.138	0.679	0.507
7	15.00	-0.267	0.575	0.409
14	11.30	-0.020	0.911	0.764
14	15.30	-0.023	0.901	0.752

Table 4 Input data for the aerodynamic method. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Wind speed ($m\ s^{-1}$) at		Air temperature (°C) at 0.3 m	Δ(air temperature) (K)	Δ(wind speed) ($m\ s^{-1}$)
		0.8 m	0.3 m			
0	11.00	5.17	4.26	8.29	0.19	-0.91
0	12.40	5.00	4.16	9.09	0.28	-0.84
0	16.00	5.12	4.24	10.26	0.19	-0.88
0	17.30	5.41	4.43	10.20	0.04	-0.98
1	14.30	3.24	2.67	8.24	0.24	-0.57
1	15.40	2.85	2.37	8.45	0.31	-0.48
2	15.50	1.82	1.56	9.79	0.43	-0.26
2	17.10	2.38	2.00	9.80	0.26	-0.38
7	12.30	1.69	1.45	10.66	0.46	-0.24
7	15.00	1.30	1.12	12.55	0.49	-0.18
14	11.30	4.26	3.68	18.03	0.41	-0.58
14	15.30	3.97	3.42	21.78	0.41	-0.55

Table 5 Input data for the Theoretical Profile method. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Wind speed at 1.30 m ($m\ s^{-1}$)
0	11.00	5.48
0	12.40	5.31
0	16.00	5.44
0	17.30	5.80
1	14.30	3.46
1	15.40	3.03
2	15.50	1.97
2	17.10	2.53
7	12.30	1.78
7	15.00	1.36
14	11.30	4.53
14	15.30	4.20

Annex 2 Concentrations of ethoprophos, tri-allate and parathion measured in air

Table 1 Concentrations of ethoprophos, tri-allate and parathion measured in air at different heights above the rectangular plot. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling	Concentration (µg m^{-3})			
	(h)	0.30 m	0.50 m	0.80 m	1.50 m
Ethoprophos					
0	12.42	12.9	10.5	4.5	2.9
0	15.56	6.9	5.5	4.1	2.3
0	17.32	4.6	3.2	2.2	1.2
1	14.30	1.1	0.9	0.6	0.4
1	15.45	1.3	1.0	0.8	0.5
2	15.52	2.2	1.7	1.1	0.6
2	17.12	1.9	1.3	1.0	0.6
7	12.32	0.14	0.11	0.10	0.07
7	14.56	0.040	0.032	0.029	0.022
14	11.26	0.76	0.60	0.42	0.26
14	15.27	0.047	0.038	0.027	0.021
Tri-allate					
0	15.56	15.9	13.1	9.9	5.3
0	17.32	9.4	6.7	4.5	2.5
1	14.30	2.4	1.8	1.2	0.7
1	15.45	2.4	1.8	1.3	0.7
2	15.52	2.7	2.1	1.4	0.8
2	17.12	2.4	1.7	1.3	0.7
7	12.32	0.36	0.27	0.22	0.16
7	14.56	0.14	0.11	0.09	0.07
14	11.26	0.74	0.59	0.43	0.25
14	15.27	0.11	0.082	0.059	0.039
Parathion					
0	11.03	1.7	1.2	1.0	0.62
0	12.42	1.1	0.85	0.47	0.30
0	15.56	0.88	0.71	0.54	0.35
0	17.32	0.78	0.43	0.32	0.19
1	14.30	0.26	0.40	0.15	0.07
1	15.45	0.34	0.25	0.19	0.10
2	15.52	0.33	0.24	0.18	0.09
2	17.12	0.30	0.22	0.17	0.09
7	12.32	0.045	0.030	0.024	0.017
7	14.56	0.012	0.010	0.007	0.005
14	11.26	0.22	0.16	0.11	0.070
14	15.27	0.016	0.013	0.009	0.008

Table 2 Concentrations of ethoprophos, tri-allate and parathion in air measured at 1.30 m above the circular plot. Measurements in duplicate. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling (h)	Concentration ($\mu g\ m^{-3}$) first	second
		Ethoprophos	
0	15.56	0.47	0.49
0	17.32	0.34	0.34
1	14.30	0.079	0.077
1	15.45	0.083	0.090
2	15.52	0.17	0.18
2	17.12	0.12	0.13
7	12.32	0.074	0.047
7	14.56	0.028	0.038
14	11.26	0.053	0.054
14	15.27	0.006	0.006
		Tri-allate	
0	15.56	1.1	1.0
0	17.32	0.57	0.67
1	14.30	0.18	0.16
1	15.45	0.18	0.17
2	15.52	0.21	0.24
2	17.12	0.15	0.17
7	12.32	0.11	0.098
7	14.56	0.071	0.070
14	11.26	0.064	0.064
14	15.27	0.016	0.016
		Parathion	
0	15.56	0.055	0.053
0	17.32	0.030	0.039
1	14.30	0.014	0.014
1	15.45	0.017	0.018
2	15.52	0.015	0.031
2	17.12	0.018	0.016
7	12.32	0.016	0.008
7	14.56	0.005	0.005
14	11.26	0.011	0.012
14	15.27	< 0.002	< 0.002

Annex 3 Areic rates of volatilization of ethoprophos, tri-allate and parathion

Table 1 Rates of volatilization of ethoprophos, tri-allate and parathion determined with the aerodynamic (AD), Bowen-ratio (BR), Theoretical Profile (TP) and Box (B) methods after their application at the Vredepeel field. The application of parathion, ethoprophos and tri-allate ended at 11.00, 12.40 and 14.50 h, respectively. Day 0 = day of application (April 6, 1993)

Day	Starting time air sampling	Flux density ($\mu g\ m^{-2}\ h^{-1}$)			
	(h)	AD	BR	TP	B
			Ethoprophos		
0	12.42	5770	5610	-	-
0	15.56	1950	1387	1567	438
0	17.32	1770	948	1147	296
1	14.30	249	208	162	66
1	15.45	253	163	157	72
2	15.52	489	324	207	98
2	17.12	358	233	190	105
7	12.32	21	21	62	37
7	14.56	5.5	3.3	27	27
14	11.26	188	259	145	27
14	15.27	11	11	15	17
			Tri-allate		
0	15.56	4179	2972	3428	1691
0	17.32	3615	1935	2156	997
1	14.30	598	500	353	212
1	15.45	516	332	318	215
2	15.52	578	383	266	227
2	17.12	437	285	243	197
7	12.32	64	64	107	88
7	14.56	24	14	57	76
14	11.26	171	236	174	44
14	15.27	27	29	40	43
			Parathion		
0	11.03	499	331	-	-
0	12.42	437	420	-	-
0	15.56	237	168	176	39
0	17.32	339	182	120	26
1	14.30	55	46	29	10
1	15.45	70	45	32	13
2	15.52	67	44	27	13
2	17.12	52	34	26	14
7	12.32	10	10	12	7
7	14.56	2.5	1.5	4.1	8
14	11.26	61	84	31	7
14	15.27	3.8	3.9	< 5	6