Volatilization of parathion and chlorothalonil after spraying onto a potato crop

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ABSTRACT

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At fourteen times after application of parathion and chlorothalonil to a potato crop their rates of volatilization were determined by the aerodynamic and Bowen ratio methods. The highest volatilization rate of parathion occurred shortly after application. In the first hours after application its volatilization rate decreased sharply; thereafter it decreased more gradually. The volatilization rate of chlorothalonil at one week after application did not differ much from that shortly after application. Weather conditions in the first twenty-four hours after application of both pesticides were simulated in a chamber. The volatilization of parathion in the chamber had the same order of magnitude as that determined in the field.

Keywords: aerodynamic method, air quality, air sampling, Bowen ratio method, gas chromatography, pesticide.

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Preface

In recent years, the environmental risks of the large-scale use of pesticides have become a matter of increasing concern. As most pesticides are applied as a spray onto soil or crop, part of the dosage can be expected to be emitted into the air during and after application. As information on the rate and extent of the volatilization of pesticides was scarce, a research project was started at the DLO Winand Staring Centre (SC-DLO) to collect data on the volatilization of pesticides after their application in the field. This research was part of the research programme of the Multi-Year Crop Protection Plan as financed 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 the emission of pesticides from soil and plant surfaces into the air during and after application.

The experiment was done in August 1993 on the experimental farm 'De Kandelaar' at Biddinghuizen (Flevoland Province). A field with a potato crop was sprayed with a mixture of parathion and chlorothalonil. The volatilization rates of these pesticides were determined with two agro-meteorological methods. The rate of decline of the pesticides on the sprayed potato leaves was also measured.

The present research was realized in co-operation with R. Kubiak, T. Maurer and T. Müller at the Staatliche Lehr- und Forschungsanstalt (SLFA) in Neustadt/W. (Germany). At the SLFA, experiments on the volatilization of pesticides are being done with a volatilization chamber, in which weather conditions can be simulated. An experiment on the volatilization of parathion from potato plants similar to that at Biddinghuizen was done at the SLFA to check whether the results obtained with the SLFA system are equivalent to those obtained in the field.

Thanks are due to F. Nieuwland of the Experimental Farm at Biddinghuizen for his permission to carry out the experiment at the experimental farm and for his 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 experiments is gratefully acknowledged.

Woord vooraf

In de laatste jaren is de bezorgdheid over de milieu-risico's van het grootschalig gebruik van bestrijdingsmiddelen toegenomen. Aangezien de meeste bestrijdingsmiddelen toegepast worden door de grond of het gewas te bespuiten, kan verwacht worden dat een deel van de dosering naar de lucht geëmitteerd wordt gedurende en na de toepassing. Omdat de informatie over de snelheid en mate van vervluchtiging schaars was, werd een onderzoeksproject gestart bij DLO-Staring Centrum (SC-DLO) om gegevens te verkrijgen over de vervluchtiging van bestrijdingsmiddelen na toepassing van deze middelen in het veld. Het onderzoek maakt deel uit van het onderzoekprogramma van het Meerjarenplan Gewasbescherming, dat gefinancierd wordt door het Ministerie van Landbouw, Natuurbeheer en Visserij. In het kader van dit programma wordt onderzoek gedaan naar de snelheid en mate van emissie van bestrijdingsmiddelen vanaf bodem- en plantoppervlakken naar de lucht gedurende en na toepassing.

Het experiment werd uitgevoerd in augustus 1993 op de proefboerderij 'De Kandelaar' bij Biddinghuizen (Provincie Flevoland). Een veld met een aardappelgewas werd bespoten met een mengsel van parathion en chloorthalonil. In dit rapport worden de resultaten gegeven over de vervluchtiging, zoals die bepaald werd met twee agrometeorologische methoden. De snelheid van afname van de bestrijdingsmiddelen op de bespoten aardappelbladeren werd eveneens gemeten.

In het huidige onderzoek werd samengewerkt met R. Kubiak, T. Maurer en T. Müller van het Staatliche Lehr- und Forschungs Anstalt (SLFA) in Neustadt/W. (Duitsland). Op het SLFA worden experimenten over de vervluchtiging van bestrijdingsmiddelen uitgevoerd in een klimaatkamer, waarin weersomstandigheden gesimuleerd kunnen worden. Een experiment over de vervluchtiging van parathion vanaf aardappelplanten analoog aan die bij Biddinghuizen werd uitgevoerd op het SLFA om na te gaan of de resultaten verkregen met het SLFA-systeem gelijkwaardig zijn aan die verkregen in het veld.

Dank is verschuldigd aan F. Nieuwland van de proefboerderij bij Biddinghuizen voor zijn toestemming om het experiment op de proefboerderij uit te voeren en voor zijn medewerking voor en tijdens het experiment. De hulp van J.H. Oude Voshaar van de DLO Groep Landbouwwiskunde bij de statistische analyse van de resultaten werd zeer op prijs gesteld.

Summary

In the last decade, the large-scale use of pesticides in agriculture has become a matter of increasing public and political concern. In arable farming, most pesticides are sprayed onto the soil or the crop. After the application of a pesticide, a fraction of the dosage evaporates into the atmosphere. Transport of pesticide by dispersion in the air results in exposure of people living in the vicinity of the site of application and this may result in adverse health effects. The deposition of pesticides from the air onto soil or water surfaces may result in adverse effects in terrestrial and aquatic ecosystems.

The rate of volatilization of pesticide from soil or plant surfaces is likely to be affected by their physico-chemical properties, such as vapour pressure and water solubility. As little information was available on the rate of volatilization of pesticide from plant surfaces, experiments were set up to collect data on the course with time of the rate of volatilization of parathion and chlorothalonil after their application to a potato crop.

At 14 times after the application of the pesticides, the concentration gradient of each pesticide above the crop was measured. Using measurements on the temperature, humidity and wind speed gradients above the crop, the rate of volatilization of each pesticide was determined with the aerodynamic (AD) and Bowen-ratio (BR) methods. The rate of decline of the fraction of the dosage of each pesticide remaining on the plant leaves was also measured.

The rate of volatilization of parathion was highest during the first few hours after its application. The hourly volatilization rate ranged up to a few percent of the dosage. As no measurements were done during the first hour after application, a substantial fraction of the dosage may have volatilized during that period. In the first seven hours after its application, there was a strong decrease in the rate of volatilization of parathion. Thereafter, the decrease was more gradual.

The cumulative volatilization loss in the first week after the application of parathion was estimated to be about 31% of its dosage. At that time, hardly any parathion was measured to remain on the potato plants. Presumably, the largest fraction of parathion was transformed. However, a fraction of the parathion in/on the plant leaves was probably not extracted with the method used, which would result in under-estimation of the fraction of parathion remaining in/on the leaves.

During the first week after application, the hourly rate of volatilization of chlorothalonil did not change very much; it was about a few hundredths percent of the dosage. As the fraction of chlorothalonil remaining on the plant leaves hardly decreased during the first week after its application, it can be expected that the volatilization of chlorothalonil continues for a prolonged period.

For the first week after the application of chlorothalonil, the cumulative volatilization loss was estimated to be about 5% of its dosage. However, because of the persistence of chlorothalonil on the potato leaves, the cumulative emission can be expected to increase substantially.

On average, the rate of volatilization of pesticide as determined with the AD method was about 0.6 times that determined with the BR method. The cause of this difference is not clear. For some periods higher volatilization rates were determined with the BR method, whereas for other periods higher rates were determined with the AD method. The difference in volatilization rate as determined with these methods could be related to differences in the atmospheric conditions.

The magnitude of the effect of weather conditions on the volatilization rate can be estimated from the volatilization rates of chlorothalonil, because the fraction of chlorothalonil remaining on the potato leaves hardly decreased during the first week after its application. A strong decrease in volatilization rate with time indicates a substantial transformation of the pesticide on the plant leaves or its uptake by the plant. This was confirmed by the rates of volatilization determined for parathion, which covered a range of two orders of magnitude.

In the volatilization chamber developed by the Staatliche Lehr- und Forschungsanstalt (SLFA) at Neustadt/W. (Germany), a similar experiment was done on the volatilization of parathion from potato plants. In this chamber, the weather conditions prevailing in the field during the first day after the application of parathion were simulated. During the second hour after application, the volatilization rate measured in the volatilization chamber was the same as that determined in the field, i.e. about 2% of the dosage. During the next four hours, there was a distinct increase in the volatilization as measured in the chamber, whereas in the field it decreased substantially. This difference may be explained by the higher relative air humidity in the volatilization chamber compared with that prevailing in the field. During the last hours of the first day, the hourly volatilization as measured in the chamber corresponded roughly to that determined in the field.

At the first day after application, the cumulative emission of parathion as measured in the volatilization chamber was 25% of the dosage. Using the AD and the BR methods, the average cumulative loss was estimated to be 9% of the dosage. However, during part of this day, air temperature and air humidity in the volatilization chamber were distinctly higher than those prevailing in the field. Therefore, a higher cumulative loss by volatilization in the chamber could be expected. The duration and intensity of daylight could not be simulated in the volatilization chamber, so transformation of pesticide by photodegradation was not possible. The lower fraction of the dosage remaining on the potato plants in the field (24%) compared to that on plants in the volatilization chamber (69%) may be explained by degradation of parathion under the influence of sunlight.

After the application of a pesticide to a crop, different processes occur which affect its fate. As their importance is uncertain, the description of the course with time of the volatilization rate of the pesticide from the crop is complex.

Samenvatting

Bij de bevolking en in de politiek is de laatste tien jaar de bezorgdheid over het grootschalige gebruik van bestrijdingsmiddelen in de landbouw toegenomen. In de akkerbouw worden de meeste middelen verspoten op de bodem of op het gewas. Na de toepassing van het middel zal een deel van de dosering door vervluchtiging in de atmosfeer terechtkomen. Transport van bestrijdingsmiddel via dispersie in de lucht leidt tot blootstelling van mensen in de omgeving van de plaats van toepassing, wat nadelige gevolgen kan hebben voor de gezondheid. Depositie van bestrijdingsmiddelen vanuit de lucht op grond- of wateroppervlakken kan leiden tot nadelige effecten op terrestrische en aquatische ecosystemen.

De snelheid van vervluchtiging van bestrijdingsmiddelen vanaf grond- of bladoppervlakken wordt waarschijnlijk beïnvloed door hun fysisch-chemische eigenschappen, zoals hun dampdruk en wateroplosbaarheid. Aangezien weinig informatie beschikbaar was over de snelheid van vervluchtiging van bestrijdingsmiddel vanaf plantoppervlakken, werd een onderzoek ingesteld naar het verloop met de tijd van de snelheid van vervluchtiging van parathion en chloorthalonil na toepassing op een aardappelgewas.

Op veertien tijdstippen na de toepassing van de bestrijdingsmiddelen werd de concentratie-gradiënt van elk middel boven het gewas gemeten. Door gebruik te maken van metingen van de temperatuurs-, luchtvochtigheids- en windsnelheidsgradiënten werd de snelheid van vervluchtiging van elk middel bepaald met de aerodynamische (AD) methode en Bowen ratio (BR) methode. De afnamesnelheid van de resterende fractie van de dosering van elk middel op het blad werd ook gemeten.

De vervluchtiging van parathion was het hoogst gedurende de eerste uren na de toepassing. De uurlijkse vervluchtiging liep op tot enkele procenten van de dosering. Aangezien geen metingen werden gedaan gedurende het eerste uur na toepassing kan een aanzienlijk deel van de dosering tijdens die periode zijn vervluchtigd. Tijdens de eerste zeven uur na toepassing van parathion nam de vervluchtigingssnelheid sterk af; daarna was de afname meer geleidelijk.

Voor de eerste week na de toepassing van parathion werd de cumulatieve vervluchtiging geschat op 31% van de dosering. Na één week was er op de aardappelplanten nauwelijks parathion over. Het grootste deel van de dosering werd waarschijnlijk omgezet. Een fractie van parathion in/op de aardappelplanten werd mogelijk niet geëxtraheerd met de gebruikte methode, wat leidt tot een onderschatting van de in/op de bladeren resterende fractie parathion.

Tijdens de eerste week na toepassing veranderde de uurlijkse vervluchtigingssnelheid van chloorthalonil niet veel; zij bedroeg enkele honderdsten procenten van de dosering. Omdat de resterende fractie van chloorthalonil op de bladeren nauwelijks afnam tijdens de eerste week na toepassing, is het waarschijnlijk dat de vervluchtiging van chloorthalonil langere tijd aanhield.

Voor de eerste week na toepassing van chloorthalonil werd de cumulatieve vervluchtiging geschat op ongeveer 5% van de dosering. Vanwege de persistentie van chloorthalonil op het aardappelblad kan verwacht worden dat de cumulatieve emissie nog aanzienlijk toenam.

Gemiddeld genomen was de vervluchtigingssnelheid bepaald met de AD-methode ongeveer 0.6 maal die bepaald met de BR-methode. Het is niet duidelijk wat de oorzaak van dit verschil is. Voor sommige perioden werd met de BR-methode een hogere snelheid bepaald en voor andere perioden met de AD-methode. De verschillen in vervluchtigingssnelheid tussen de methoden kunnen gerelateerd zijn aan verschillen in atmosferische condities.

De grootte van het effect van de weerscondities op de vervluchtiging kan geschat worden met behulp van de vervluchtigingssnelheden van chloorthalonil, omdat de fractie chloorthalonil resterend op het aardappelblad nauwelijks afnam in de eerste week na toepassing. Een sterke afname in de vervluchtigingssnelheid met de tijd duidt op een aanzienlijke omzetting van het middel op de bladeren of op opname door de plant. De snelheden van vervluchtiging bepaald voor parathion, die een traject bestreken van twee ordes van grootte, bevestigen dit.

In de klimaatkamer die het Staatliche Lehr- und Forschungsanstalt (SLFA) in Neustadt/W. (Duitsland) heeft ontwikkeld, werd een vergelijkbaar experiment naar de vervluchtiging van parathion vanaf aardappelplanten uitgevoerd. In deze kamer werden de weerscondities in het veld gedurende de eerste dag na de toepassing van parathion nagebootst. Tijdens het tweede uur na toepassing was de vervluchtiging gemeten in de klimaatkamer gelijk aan die bepaald in het veld: ongeveer 2% van de dosering. In de volgende vier uur werd een toename in de vervluchtiging gemeten in de klimaatkamer, terwijl die in het veld duidelijk afnam. Dit verschil is mogelijk te verklaren door de hogere luchtvochtigheid in de klimaatkamer in vergelijking met die in het veld. Tijdens de laatste uren van de eerste dag kwam de in de klimaatkamer gemeten uurlijkse emissie ruwweg overeen met die in het veld.

Voor de eerste dag na toepassing bedroeg de in de klimaatkamer gemeten cumulatieve vervluchtiging van parathion 25% van de dosering. Het met de AD en BR methoden geschatte cumulatieve verlies bedroeg 9% van de dosering. Gedurende een deel van de dag waren de luchttemperatuur en luchtvochtigheid in de klimaatkamer beduidend hoger dan die in het veld, zodat een hogere cumulatieve vervluchtiging verklaarbaar is. De duur en de intensiteit van het daglicht kon in de klimaatkamer niet nagebootst worden, zodat de fotochemische omzetting van het middel niet mogelijk was. De lagere fractie van de dosering die resteerde op de aardappelplanten in het veld (24%) ten opzichte van die op planten in de klimaatkamer (69%) is mogelijk te verklaren door omzetting van parathion onder invloed van zonlicht.

Na de toepassing van een bestrijdingsmiddel op een gewas zijn er verschillende processen die zijn lotgevallen bepalen. Omdat het belang van de processen moeilijk is in te schatten, is de beschrijving van het verloop van de snelheid van vervluchtiging van het bestrijdingsmiddel vanaf het gewas met de tijd complex.

1 Introduction

In the last decade, the large-scale use of pesticides in agriculture has become a matter of increasing public and political concern. As most pesticides are sprayed onto the soil surface or onto the crop, a fraction of the dosage can be lost by volatilization during and after application. Exposure of people living in the vicinity to concentrations of pesticides in air may result in adverse health effects. Deposition of pesticides onto neighbouring fields and water courses results in exposure of terrestrial and aquatic organisms to these pesticides and this may cause adverse effects.

The rate of volatilization of pesticides from soil and plant surfaces is likely to be affected by their physico-chemical properties. Pesticides with comparatively high vapour pressure, such as EPTC, can be expected to volatilize fairly rapidly after spraying. Pesticides with comparatively low vapour pressure, such as atrazine, can be expected to volatilize at a low rate. However, the volatilization rate may also be affected by the partitioning of the pesticide between the gas and liquid phases and that between the liquid and solid phases. As the moisture condition of the soil and plant surfaces can change substantially with time, large differences in the course of the rate of volatilization of pesticide with time could be expected.

Laboratory methods have been used to collect data on pesticide volatilization. Dörfler et al. (1991) measured the volatilization of atrazine and lindane from turnip, oats and beans in a volatilization chamber (20 °C; wind speed of 0.05 m s^{-1}) during the first 24 h after their application. The half-lives on the plants ranged from 0.3 to 0.6 days for lindane and from 15 to 26 days for atrazine. Kubiak et al. (1993a) measured the volatilization of ^{14}C-labeled isoproturon from a 0.5 m^2 plant stand in a volatilization chamber during the first 24 hours. The plants were kept in the dark at 20 °C and the wind speed was 1.1 m s^{-1}. Under these conditions, about 0.7% of the dosage volatilized. Kubiak et al. (1995) simulated the conditions after a field application of methyl parathion to beans in the volatilization chamber. The volatilization rate of methyl parathion in the field as estimated from the course with time of its residue on the plants corresponded with that measured in the volatilization chamber. However, it is not certain whether the volatilization rate as measured in the volatilization chamber represented the actual rate in the field.

Comparatively few experiments have been done to measure the rate and extent of volatilization of pesticides from plant surfaces in the field. Taylor et al. (1977) measured the course with time of the rate of volatilization of dieldrin and heptachlor after application to grass land. At several times, the volatilization rate was measured with the aerodynamic method. The highest rates of volatilization were measured shortly after application; they decreased sharply thereafter. About 45% of the dosage of heptachlor and about 12% of the dosage of dieldrin was lost during the first day. The course of the volatilization rate with time showed a diurnal pattern. After the first four weeks, only comparatively small fractions of the dosages remained.

Different methods have been used to determine the volatilization rates in the field. Parmele et al. (1972) determined the volatilization rates of dieldrin and heptachlor above a corn crop (0.75 m high) with the aerodynamic and Bowen ratio methods. The flux densities as determined with both methods during the day were similar, but the measurements in late afternoon were distinctly different. These differences may have been caused by the relatively large inaccuracy in the Bowen ratios as measured during those hours.

A field experiment was set up to collect data on the emission of parathion (insecticide) and chlorothalonil (fungicide) into the air after application to a potato crop. Parathion is a moderately volatile pesticide, its saturated vapour pressure at 20 °C being 0.89 mPa (Tomlin, 1994). There are conflicting data on the vapour pressure of chlorothalonil at 25 °C, varying from 0.076 mPa (Tomlin, 1994) to 26 mPa (Genderen and Van Ekeren, 1993). Some other physico-chemical properties of parathion and chlorothalonil are presented in Table 1.

At five times after application, the rate of volatilization of the pesticides from the potato crop was measured with two agrometeorological methods, i.e. the aerodynamic method and the Bowen ratio method (Section 3.1). Further, the rate of decline of the deposit of each pesticide on the potato leaves was measured.

At the Staatliche Lehr- und Forschungsanstalt (SLFA) in Neustadt/W. (Germany), research on pesticide volatilization is being done with a volatilization chamber, in which weather conditions can be simulated. Using this chamber, Kubiak et al. (1995) measured the volatilization rate of methyl parathion from beans under conditions approaching those in the field, but the rate in the field was not measured directly in the atmosphere as a check. An experiment on the volatilization of parathion was done with the SLFA system under conditions similar to those at Biddinghuizen. The weather conditions during the first day after the field application were approached as much as possible. The results on the rate and extent of the volatilization of parathion, as measured in the laboratory (Section 3.2), are compared with those measured in the field (Section 4).

An attempt is made to relate the volatilization rates of parathion and chlorothalonil measured in the field to their physico-chemical properties and to the prevailing weather conditions. The contribution of the fraction of each pesticide volatilized to its mass balance is discussed (Section 4).

Table 1 Some physico-chemical properties of chlorothalonil and parathion at 20 °C (from Tomlin, 1994)

Pesticide	Molecular mass (g mol^{-1})	Water solubility (mg L^{-1})	Ratio air/water
Chlorothalonil	265.9	0.9[a]	$9.1 \cdot 10^{-6}$ [a]
Parathion	291.3	11	$9.8 \cdot 10^{-6}$

[a] At 25 °C.

2 Material and methods

2.1 Field experiment

2.1.1 Description of the field and the application of pesticides

A rectangular field of about 2,5 hectares (260 m by 96 m) with a full-grown potato crop (Agria cultivar) was selected near Biddinghuizen (Flevoland Province). The area in which the field is located has an open landscape with only few obstacles. Wind obstacles such as houses and trees would disturb the dispersion pattern of pesticide vapour in the air above and around the treated field.

The average height of the crop above the top of the ridges was 0.5 m. The height of the ridges was about 0.2 m. The potato field was surrounded on all sides by other fields with a potato crop in a growth stage similar to that of the field studied. At a distance of about 700 m to the west there was a farm house. In all other directions there was arable land over a distance of at least a few kilometres. The location of the field is indicated in Figure 1.

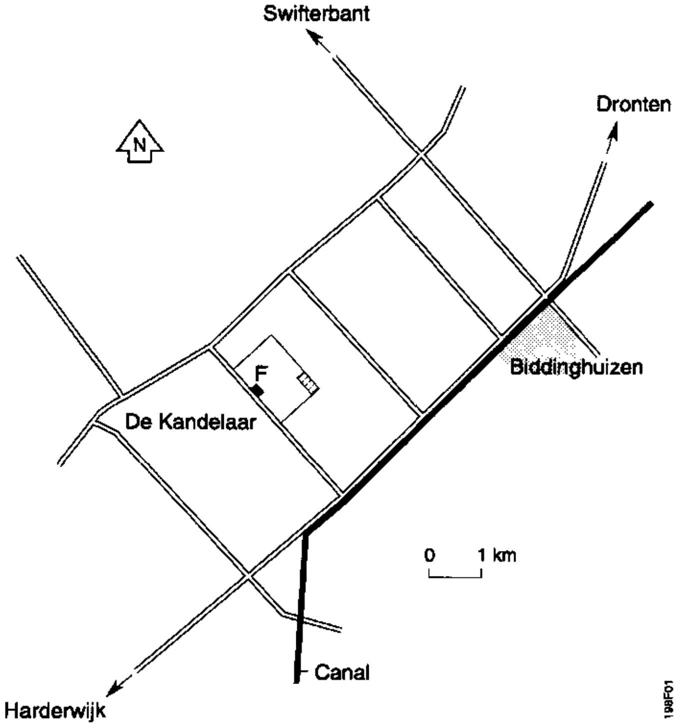

Fig. 1 Location of the field with the potato crop treated with parathion and chlorothalonil.
▨ *= treated field. F = farm house*

A Douven field-spraying machine was used. The working width of the sprayer was 24 m and it was equipped with 48 Teejet nozzles (type XR 110 03), so the distance between two adjacent nozzles was 0.5 m. The day before the application of parathion and chlorothalonil, this equipment was checked and the rate of spraying of each nozzle at the pressure used during application was measured with water. The water released from each nozzle during 1 min was collected and weighed. The average release was measured to be 0.995 L min^{-1} (n = 12, s.d. = 0.019). More detailed information on the rates of spraying of the nozzles are presented in Annex 1.

Tests were done in the laboratory to check whether the formulated products could be applied as a mixture. The mixture of both formulated products in water was found to be stable; there was no distinct visual reaction (e.g. sedimentation).

The intended rates of application were 4 L of formulated parathion (Luxan parathion 25%, 0.25 kg parathion per litre) per hectare and 3.5 L of formulated chlorothalonil (Daconil 500 flowable, 0.5 kg chlorothalonil per litre) per hectare. Shortly before the application, the spraying solution was prepared by mixing 12 L formulated parathion and 11 L formulated chlorothalonil with 695 L water.

The potato crop was sprayed on August 18, 1993, starting at 12.36 h. During spraying, the average driving speed was measured to be 4.9 km h^{-1} and the spraying pressure was 260 kPa. From the rate of spraying from the nozzles and the driving speed of the apparatus, the application rate of the spraying solution was calculated to be 245 L ha^{-1}. The height of the nozzles above the crop ranged between 0.4 and 0.6 m. The spraying ended at 12.55 h. By multiplication of the calculated concentration of each pesticide in the spraying solution with the application rate of this solution, the areic masses of parathion and chlorothalonil applied were obtained, i.e. 1.06 and 1.94 kg ha^{-1}, respectively. In the interpretation of the results, these values were used to express the rate of volatilization as a percentage of the dosage of pesticide per hour.

The concentration of each pesticide in the spraying solution was checked by taking samples of this solution. A first sample was taken from the spraying solution in the tank before the start of the application; a second sample was taken from this solution at the end of the application. Three more samples were taken from the solution sprayed from the outermost nozzle at the beginning, halfway through and at the end of the application. Subsamples of 500 μL were taken in the field and added to glass flasks with 50 mL of an ethyl acetate/hexane mixture (50/50 v/v). The flasks were shaken manually for a few min and subsequently shaken with a mechanical shaker in a barn of the experimental farm for 30 min (at a frequency of about 130 cycles per min). The concentration of parathion in these samples amounted to 93% (n = 5, s.d. = 1.3%) of the concentration in the spraying solution as calculated from the volume of spraying liquid and the fraction of active ingredient in the volume of formulated product added. For chlorothalonil, there was a difference between the concentration in the samples taken from the tank solution and those taken from the liquid sprayed from the outermost nozzle. The concentration measured in samples from the tank was 93% (n = 2) of that calculated from the mass of chlorothalonil in the formulated product and the volume of spraying liquid, whereas the concentration measured in samples taken from liquid sprayed from the outermost nozzle was 81% (n = 3, s.d. = 4.0) of the concentration calculated. It should be noted that the results of the analysis of standard solutions of chlorothalonil showed a greater variation than those of the analysis of standard solutions of parathion. As the concentrations measured corresponded reasonably well with those calculated from the content of pesticide in the formulated product, no correction on the areic masses applied was considered necessary.

2.1.2 Determination of the rate of volatilization

The aerodynamic and Bowen ratio methods were used to determine the source strength of the emission of parathion and chlorothalonil into the air after application. The aerodynamic (AD) method is based on the Thornthwaite-Holzmann equation. The rate of volatilization of pesticide into the air is proportional to the difference in the concentration of pesticide in air over a certain height interval and the difference in wind speed over the same interval. Further, the calculated rate is corrected for the stability of the surface air layer. For the calculation of the correction factor, empirical relations with the Richardson number as stability parameter have been derived (See Majewski et al., 1990). Using the AD method, an upwind fetch (i.e. the length of treated area upwind) is required of at least 100 times the greatest height above the soil surface at which an air sample is taken to measure the concentration of pesticide in the air (Majewski et al., 1990). More detailed information on the AD method is given by Majewski et al. (1989, 1990). In this study, the concentration of each pesticide in air was measured at four heights above the treated crop. At the same heights, the wind speed was measured.

The Bowen ratio (BR) method is based on the assumption that the coefficient for the dispersion of sensible heat is the same as that of the pesticide. The flux density of sensible heat is calculated from measurements on the energy balance at the earth's surface. The Bowen ratio coefficient, i.e. the ratio between the latent and sensible heat flux densities, is calculated by dividing the temperature gradient by the water vapour pressure gradient and multiplying it by the psychrometer constant. From the Bowen ratio coefficient and the measured soil heat and net radiation flux densities, the sensible heat flux density is calculated. The coefficient for the dispersion of sensible heat is calculated by dividing the sensible heat flux density by the vertical air temperature gradient measured. The rate of volatilization of pesticide is calculated from this coefficient and the measured vertical pesticide concentration gradient in air. More detailed information on the BR method is given by Majewski et al. (1990). In the present study, the net radiation was measured at a height of 1.5 m above the top of the potato ridges. As the soil heat flux density is measured at a depth of 0.08 m, a correction needs to be made to take account of the heat stored or released in the top 0.08 m layer, thereby enabling to calculate the soil heat flux density at the soil surface. In this calculation procedure, an average soil bulk density was assumed of 1 150 kg m^3 and the average soil moisture content was estimated to be 27%.

For each pesticide, a regression model with the factors method and measurement times was used to check whether there was a difference between the methods. As multiplicative effects were expected, the analysis was made using the logarithm of the volatilization rate. Moreover, this resulted in stabilization of the variances. The analysis was made with Genstat 5.3.1.

2.1.3 Rate of decline on potato leaves

The surface area of the treated field was divided into four sections of identical size to make the sampling of the plant leaves and their subsequent extraction easier. Before the application, samples of the plant leaves were taken to measure any residue of the pesticides on this crop. No substantial amounts of parathion and chlorothalonil were measured in these samples.

The initial areic masses of the pesticides on the potato leaves were measured. Before the application, in each section one tempex plate (1.0 m by 0.1 m) was placed horizontally at crop height. On each plate ten potato leaves were placed, with the leaf surface in a horizontal position. Directly after the application, the sprayed leaves were pooled per plate and put into 600-mL glass flasks. A volume of 100 mL of a mixture of ethyl acetate and hexane (50/50 v/v) was added to each flask. The flasks were sealed with Teflon tape and plastic cap. The flasks were left overnight at room temperature and then shaken for 10 min at a rate of about 110 cycles min^{-1}. A part of the supernatant solution in each flask was transferred into another glass flask with screw cap (with aluminium foil inlay) and was dried with anhydrous sodium sulphate. These samples were stored in deep freeze until analysis.

The rate of decline of pesticide on the potato leaves was measured by taking plant samples at several times after application. They were taken at 1, 4, 7 and 26 hours after application and on the 2nd, 3rd and 7th days after the day of application. The plant samples consisted of top leaves which were most likely fully exposed to the spraying with the pesticides. In each field section, three samples were taken consisting of 15 leaves each. The extraction procedure of these samples was the same as that for the samples taken to determine the initial areic mass of pesticide on the potato leaves.

2.1.4 Measurement of the pesticides in air

The concentrations of parathion and chlorothalonil in air were measured by sampling the air using a vacuum pump (Siemens, type ELMO-G, 1.1 kW). The pressure in the air sampling system was measured with a SERVO manometer. The rate of sampling was adjusted with flow meters (Brooks, variable area type 8-1307-V, range 8 - 80 L min^{-1}). The total air volume per sample was measured using gas meters (Schlumberger, type G 4-220, capacity 100 L min^{-1}). A diagram of the sampling unit and its connections is given in Figure 2. The instruments were placed in an

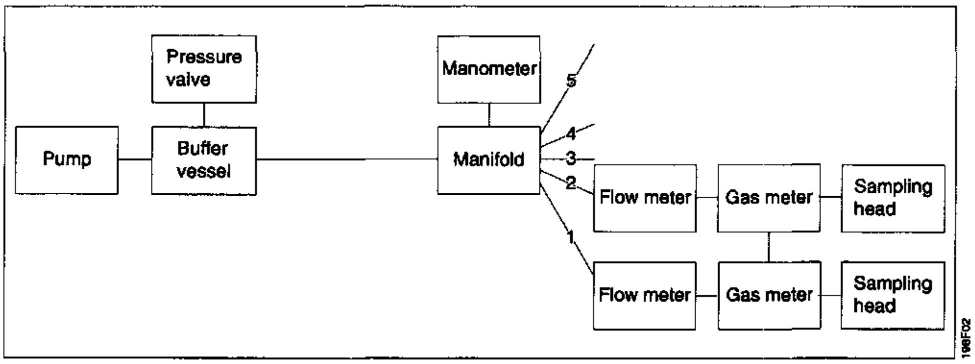

Fig. 2 Diagram of connections of the sampling unit

aluminium housing. Power for the air sampling equipment was supplied by a power aggregrate (Robin, type RGX 3500, 3 kW).

The air sampling equipment upwind of the treated field consisted of a vacuum pump (KNF Neuberger, type NO 135 ANE, 0.4 kW), a flow control valve, a buffer vessel (with a manometer) and a gas meter (Schlumberger, type G 4-220, capacity 100 L min^{-1}), placed in series in this sequence. The instruments were placed in a wooden housing. The inlet of the gas meter was connected with the sampling tube by plastic tubing. The power for this equipment was supplied by a car battery (158 kC).

The suitability of XAD-4 as adsorbent to measure parathion and chlorothalonil in air was checked in the laboratory. A solution of each pesticide of 100 mg L^{-1} was prepared in ethyl acetate. From this solution, 50 µL samples ($n = 3$) were put into sampling tubes containing 10 g XAD-4 each. Each volume of 50 µL was divided into ten droplets, which were spread over the top surface of the XAD layer. To one of the sampling tubes a second tube with 5 g XAD-4 was connected as a check on breakthrough from the first tube. Subsequently, air was drawn through the sampling tubes at a rate of 3 m^3 h^{-1} for about 1 h at an average air temperature and humidity of 23 °C and 72%, respectively. The contents of each sampling tube were extracted by shaking with 90 g ethyl acetate for 30 min (at a frequency of 130 cycles per min). For the analysis of parathion and chlorothalonil in these extracts, 3 µL subsamples were injected into a gas chromatograph with electron-capture detector. More details on the analytical procedure are given in Section 2.1.6. The recovery of parathion was measured to be 101.9% ($n = 3$, s.d. = 0.8) and that of chlorothalonil was measured to be 100.3% ($n = 3$, s.d. = 1.7). No breakthrough of parathion and chlorothalonil from the first tube into the second tube was measured.

In the field, air samples were taken at a rate of 50 L min^{-1} for one or two hours using glass tubes (about 35 mm inner diam.) filled with XAD-4 (SERVA, 30 mL, grain diam. 0.3 - 1.0 mm). The samples were taken at 0.8, 1.0, 1.3 and 1.5 m above the top of the ridges. On the day of application, four series of one-hour air samples were taken, starting at 1.0, 2.7, 4.1, and 6.0 hours after application. On the first day after the day of application, four series of one-hour air samples were taken, starting at 21, 24, 28 and 29 h after application. On the 2nd and 3rd days after the day of application, two series of one-hour air samples were taken each day, starting at 49, 50, 75 and 76 h after application. On the 7th day after application, two series of two-hour air samples were taken, starting at 167 and 169 h after application. For each air sampling series, a second tube was placed in series with the sampling tube at 1.0 m above the ground as a check on breakthrough of the pesticides. More detailed information on the air sampling tubes has been given by Bor et al. (1995).

During each sampling period, an air sample was taken at a site at an upwind distance of a few tens of metres from the treated field at a height of about 1.5 m above the ground. The air samples were taken at a rate of about 40 L min^{-1}. They were taken to assess whether there were sources of emission upwind of the treated field which affected the concentrations of parathion and chlorothalonil in the air measured downwind of the field.

The content of each sampling tube was transferred into a 250-mL glass flask (type Schott) with screw cap (with aluminium foil inlay). As the extracts of chlorothalonil in ethyl acetate could not be stored for a comparatively long period, the air samples were extracted with a mixture of ethyl acetate and hexane (50/50 v/v). The sampling tube was rinsed with about 30 g of the mixture of ethyl acetate and hexane and this liquid was added to the same flask. Then a mass of the same solvent mixture was added to the flask, until the total mass of the liquid in the flask was about 100 g. The exact mass of liquid added to each flask was obtained by weighing. The flasks were shaken for 30 min at a rate of about 110 cycles min^{-1}. Subsequently, the supernatant solution in each flask was transferred to another 250-mL glass flask (type Schott) with screw cap (with aluminium foil inlay) and these samples were stored in deep freeze until analysis. Because the concentrations of the pesticides in the extracts from the samples taken on the 7th day after the day of application were low, the extracts of these samples were concentrated. The flasks with extracts were placed in a water bath at 35 °C and a flow of N_2 was maintained until all solvent was evaporated. The residu in each flask was dissolved by adding to each flask 1 mL of a mixture of hexane and ethyl acetate (50/50 v/v).

2.1.5 Meteorological measurements

A tripod with cup anemometers and a wind vane was placed in the treated field. The level of the top of the ridges was taken as the reference level for the measurements. The wind speed was measured with cup anemometers (Vector Instruments, type A100R) at four heights: 0.5, 0.8, 1.3 and 2.0 m. The wind direction was measured with a wind vane (Vector Instruments potentiometer, type W200P) at 2.6 m. The dew point of the air was measured at 0.8 and 1.3 m above the ground with a chilled mirror hygrometer (General Eastern, type Dew-10). The air temperature was measured at the same heights with chromel-constantan thermocouples (diam. 0.01 cm). The soil heat flux was measured with two heat flow transducers (Radiation and Energy Balance Systems Inc., type HFT-1). The net radiation was measured with a net radiometer (Radiation and Energy Balance Systems Inc., type Q^*6). The course with time of these meteorological variables was registered with a Campbell Scientific 21X micrologger. The power for the datalogger was supplied by car batteries (Varta, 252 kC).

The soil temperature was measured at depths of 0.05 and 0.15 m in a potato ridge and at a depth of 0.05 m in a furrow. The rainfall was measured with a tipping bucket rain gauge at a site next to the test field. At each hour, the data on soil temperature and rainfall were recorded with a Tattle datalogger. Power for this datalogger was supplied by six internal 1.5 V batteries (type Jumbo). At the end of the experiment, the content of the rain gauge was transferred into a measuring flask, which enabled the calculation of the thickness of the layer of rain water corresponding to one pulse recorded with the datalogger.

2.1.6 Chemical analysis

Two methods were used to analyse the extracts with the pesticides. In the first method, samples of 3 μL from the extracts were injected into a gas chromatograph (Hewlett Packard type 5890) at 240 °C. The injection mode was splitless. The wide-bore fused-silica column (length 25 m; internal diameter 0.53 mm; film thickness 5.1 μm) contained poly-siloxane (CP-Sil 5 CB) as stationary phase. The column temperature was 240 °C. The flow rates of the carrier gas (He) and the make-up gas (N_2) were 10 and 20 mL min^{-1}, respectively. Chlorothalonil and parathion were detected with a thermionic nitrogen-phosphorus detector. The detector temperature was 280 °C. The flow rates of hydrogen and medicinal air through the detector were 3.5 and 90 ml min^{-1}, respectively. The response was recorded and processed with Multichrom (Fisons Instruments software). The retention times of chlorothalonil and parathion in this system were 2.7 and 4.0 min, respectively.

In the second method, samples of 3 μL from the extracts were injected into a gas chromatograph (Hewlett Packard type 5890) at 250 °C. The injection mode was splitless. The medium-bore fused-silica column (length 25 m; internal diameter 0.25 mm; film thickness 1.2 μm) contained poly-siloxane (CP-Sil 5 CB) as stationary phase. For 1.5 min after injection, the column temperature was 140 °C. Thereafter, the temperature increased at a rate of 45 °C min^{-1} to 240 °C. The temperature remained at this level for the next 5.3 min. Thereafter, the temperature increased again at a rate of 45 °C min^{-1} to 290 °C. The flow rates of the carrier gas (N_2) and the make-up gas (He) were 2 and 58 mL min^{-1}, respectively. Chlorothalonil was measured by electron capture using a ^{63}Ni detector. The detector temperature was 325 °C. The data were recorded and processed with Multichrom (Fisons Instruments software). The retention times of chlorothalonil and parathion under these conditions were 8.3 and 10.3 min, respectively.

Chlorothalonil and parathion in the extracts of the plant leaves were analysed with the first method, except that the injection temperature was somewhat higher: 260 °C. Chlorothalonil in the XAD extracts was analysed with the more sensitive second method, because of the comparatively low concentrations of chlorothalonil in these extracts. For the analysis of parathion in the XAD extracts of the samples taken on the day of application and on the first and second days thereafter, the first method was used. For the analysis of parathion in the XAD extracts of the samples taken on later days, the more sensitive second method was used.

2.2 Laboratory experiment

2.2.1 Equipment

2.2.1.1 Application chamber

For the application of labeled pesticides to plants, a chamber (1.50 m high, 1.00 m wide, 0.80 m deep) was constructed. Plants are placed on a stainless steel platform (surface area 0.8 m^2) with a net experimental surface area of 0.5 m^2. The platform is placed in the application chamber on a platform holder, the height of which can be adjusted. A nozzle is attached to a stainless steel tube (length 0.10 m), which passes through the centre of the roof. The other end of the tube is connected by stainless steel tubing to a 150 mL cylinder with spraying solution. The nozzle can be moved along a rail from one side of the chamber to the other side.

The spraying pressure and the speed of the horizontal movement of the nozzle can be regulated, which enables a wide range in application rates. A schematic view of the application chamber is presented in Figure 3. More details on the application chamber have been presented by Kubiak et al. (1993a and 1993b).

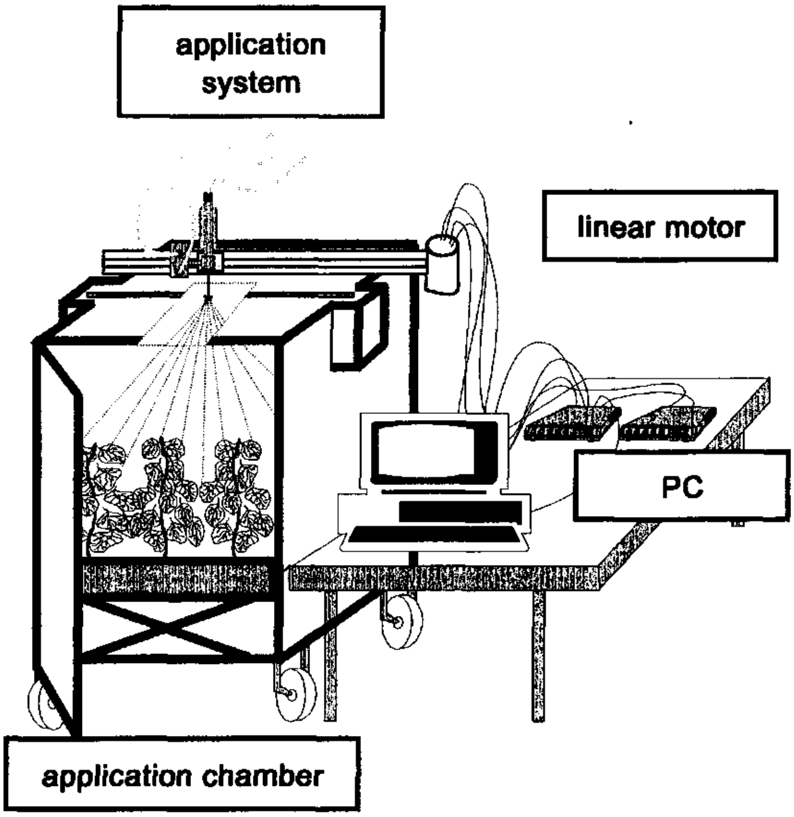

Fig. 3 View of the application chamber

2.2.1.2 Volatilization chamber

For the measurement of the rate of volatilization of the pesticide, the sprayed plants are transferred into a volatilization chamber (1.30 m high, 1.00 m wide, 0.80 m deep). A view of the volatilization chamber is presented in Figure 4. The relative humidity and temperature of the incoming air are controlled and they can be adjusted with an air-conditioning system. Before entering the volatilization chamber, the air stream passes an equalization chamber, where the turbulences caused by the transport are calmed down and converted into two parallel air streams, i.e. an upper and a lower horizontal air stream. With these two air streams simultaneously going through the volatilization chamber, but at different velocities, the vertical wind speed profile in the field is simulated. The faster upper air stream passes over the plant stand; the speed of this stream can vary between 0.4 and 2.5 m s^{-1}. The height of the air layer between the plant stand and the roof is 0.1 m. The slower lower air stream passes through the plant stand; the speed of this stream can vary between 0.1 and 0.3 m s^{-1}. The speeds of both air flows during the experiment can be adjusted by introducing the values on the required wind speeds into a computer programme with which the conditions inside the chamber are controlled. In the present experiment, the plants were kept in the dark. More details on the volatilization chamber are given in Kubiak et al. (1993a and 1993b).

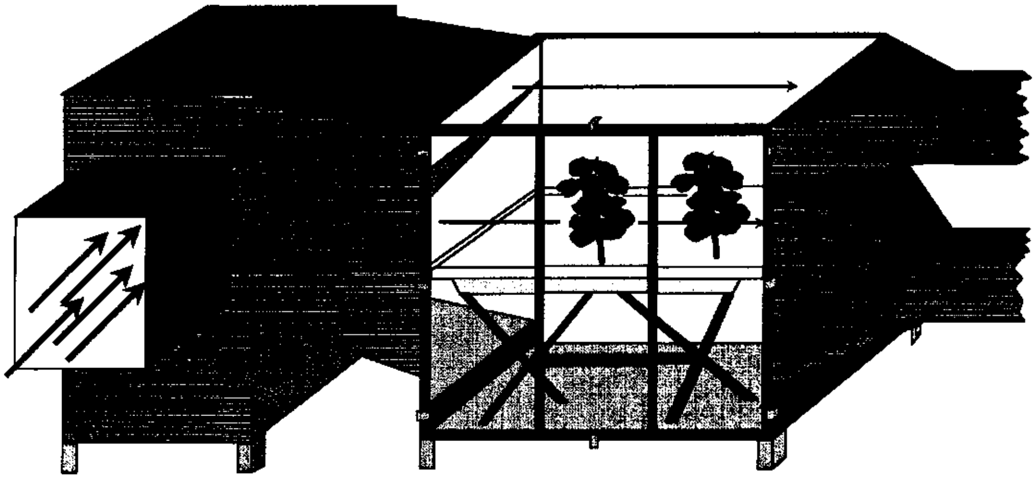

Fig. 4 View of the volatilization chamber

2.2.2 Application of parathion

Potato plants (cultivar Surprise) were grown at about 17 °C in flower pots in a glasshouse. Before the plants were placed in the application chamber, the soil under the plants, the experimental platform and the walls of this chamber were covered with paper (Schleicher and Schuell, type 597). Six potato plants with a height of about 0.50 m were placed on the experimental platform, which was placed in the application chamber. The distance between the nozzle and the top of the plant surfaces was about 0.50 m.

For the present application, a Tee Jet nozzle (type XR 110 03 VS) was mounted in the chamber. The spraying system and the rate of release of liquid from the nozzle was checked visually before application, using an 1.0 g L^{-1} aqueous solution of reinblau (Fluka). The spraying pressure and the speed of movement of the nozzle were similar to those in the field experiment.

The intended dosage of parathion was the same as that applied in the field, i.e. 1 kg ha^{-1}. A spraying solution was prepared by mixing 0.3504 g of a solution of ring ^{14}C-labelled parathion in acetone (2.54 mg parathion per litre, specific activity 90.0 µCi mg^{-1}) with 23 mL water. From the density of acetone (0.8 g mL^{-1} at 20 °C), the mass of parathion in this solution is 1.11 mg. Subsequently, 0.364 mL of formulated product (E 605, containing 0.25 kg parathion per litre) was added to the spiked aqueous solution. The radioactivity of the spraying solution was measured to be 3135.14 kBq, which corresponded to 92.11 mg parathion.

During spraying at a pressure of 250 kPa, with a rate of release of liquid of 1.00 L min^{-1}, the nozzle was moved from one side of the chamber to the other at a speed of 3.1 km h^{-1}. At this speed and at this rate of release, the resulting application rate was practically the same as that applied in the field, 234 vs. 245 L ha^{-1}. Two minutes after the application, the application chamber was opened and the experimental platform was transferred to the volatilization chamber.

The paper covers of the walls of the application chamber and the cover of the experimental platform were put into a stainless steel 30-L vessel. Subsequently, about 7.6 kg (9.6 L) acetone (technical grade) was added to submerge the covers in this liquid. The covers were extracted by stirring the acetone a few times during one day. The acetone was removed and the paper covers were extracted a second time with 9.0 kg (11.4 L) acetone in a similar way. The paper cover of the soil was placed into a vessel, to which 1.32 kg (1.7 L) acetone (technical grade) was added. This cover was extracted by mechanical shaking (Janke and Kunkel, type H S 500). After removal of the acetone, the cover was extracted once more by shaking with 1.27 kg (1.6 L) acetone.

The walls of the application chamber were decontaminated with Kleenex paper tissues dipped in acetone. After drying at 20 °C, these tissues were pressed into pellets, which were subsequently combusted with an oxidizer (Canberra-Packard, type 307). The $^{14}CO_2$ released was collected with Carbosorb (Canberra-Packard), which was subsequently mixed with permafluor (Canberra-Packard) as scintillator. After cooling these samples to room temperature, the amount of radioactivity in each sample was measured with a liquid scintillation analyzer (Packard 2550 TR/LL).

The sprayer was rinsed twice with 20 mL acetone (technical grade). Thereafter, the sprayer was dismantled and the different parts were placed in a 1000-mL beaker filled with 0.393 kg (496 mL) acetone (technical grade). The radio-active residues in other materials (e.g. flask, funnel) used for the application were removed by rinsing with 0.637 kg (804 mL) acetone, which was collected in a 1000-mL glass beaker.

From each extract, a 1 or 5 mL sample (in duplicate) was taken and transferred into a 10 or 20 mL vial. After addition of 3 or 10 mL of Ultima Gold XR (Packard) as scintillator, the radioactivity in the extracts was measured with a liquid scintillation analyzer (Packard 2550 TR/LL). The limit of determination of radioactivity in the extracts was 1.7 Bq, which corresponded with 12 ng parathion.

The radioactivity remaining in the spraying system, that remaining on the paper covers of the walls of the application chamber, that adsorbed onto the walls of the application chamber and that remaining on the paper cover of the soil were measured to be 87.46, 2000.37, 2.68 and 68.94 kBq, respectively. The radioactivity remaining in the glassware was measured to be 92.17 kBq. Thus, the total loss of radioactivity during application amounted to 2251.62 kBq, which corresponds to 66.15 mg parathion. The radioactivity applied to the plants was calculated by subtracting the total loss in radioactivity during application from the total radioactivity in the spraying solution. The total radioactivity applied to the plants was calculated to be 621.73 kBq, which corresponds with 18.27 mg parathion.

The purity of the spraying solution was checked by thin-layer chromatography. A 10 μL subsample of the spraying solution was applied onto a chromatography plate (Merck, Kieselgel 60 F 254, 0.2 mm thick) using a Linomat IV (Camag). The elution solvent was a mixture of n-hexane and ethyl acetate (70 : 30 v/v). The plate was eluted for 30 min at 20 °C. The relative retention time of parathion under these conditions was 0.47. The resulting radio-thin-layer chromatograms were recorded with a Linear Analyzer Tracemaster 40 model LB-283 (Berthold). The radioactivity originating from parathion was measured to be 94% of the total radioactivity measured.

2.2.3 Meteorological data

The meteorological data for the experiment with the volatilization chamber were taken from the data collected during the first day after the spraying of parathion on the potato crop near Biddinghuizen (Flevoland Province, See Section 2.1). During the experiment, measurements were done on the actual meteorological conditions in the volatilization chamber. The wind speed, the temperature and the relative humidity of the air of the upper air stream were measured just before it entered the volatilization chamber. The wind speed was measured with an air velocity transducer (TSI inc, type 8450). The air temperature and the air relative humidity were measured with a temperature sensor (Phillips, type CA 65250) and a humidity sensor (Testoterm, type Hygrotest).

2.2.4 Measurement of the rate of volatilization

Just like the air streams entering the volatilization chamber, the outgoing air was split into two parts. One part passed through an upper channel and the other part through a lower channel. The size of the channels was similar to those leading into the volatilization chamber. The flow rate in the upper channel was calculated from the pressure difference before and after a valve installed in this channel. This difference was measured with a pressure transducer (Setra Systems, Type 0239-12,7).

From the air flow in each channel, a fraction was drawn isokinetically into a subchannel by adjusting the speed of the air flow through the opening of the inlet of the subchannel to that of the surrounding air with a flow control probe (Guth). The air was drawn through these subchannels with vacuum pumps (Rietschle). A VFT 60 type pump was used for the upper subchannel and a VFT 40 type pump for the lower subchannel. In each subchannel, one glass cartridge was placed containing three pieces of polyurethane foam (Ziemer, type GA 3035, diam. 100 mm, length 50 mm) each. The second and third foams were used as checks on breakthrough of the first and second foams, respectively.

After the air flow had passed the 3rd polyurethane foam of each subchannel, a fraction of the flow in the subchannel was led into another subchannel with water vapour traps and CO_2 traps. The water vapour was removed with a Vigreux column in each channel, which was cooled with ethanol in a cryostate (Haake, type F3-K). The condensation water was collected in glass flasks. The remaining water vapour was removed by cooling the air in a cryostate bath (Haake, type N3-R). The nearly water-free air passed four glass cylinders (height 340 mm, inner diam. 800 mm) in series, each filled with a mixture of diethylene-glycole-monobutyl ether, ethanolamine, ethylene-glycole and phenyl-ethylene amine (1 : 1 : 1 : 1, v/v/v/v) to absorb the CO_2 present in the air stream. On top of each cylinder, a backflush cooling column was placed. The cooling liquid was ethanol at a temperature kept constant with a cryostate (Haake, type N3-R). Between the first and second glass cylinder, a silicagel (Fluka) column was placed to remove remaining water. Thereafter, the flow rate of the air through this subchannel with traps was measured with a gas meter (Elster, type G4/G6). The remainder of the air flow which had passed the three polyurethane foams in series was measured with a Quantometer (Elster, type QA25 G).

The remaining fractions of the air flowing through the lower and upper channels were combined. Subsequently, the remaining radioactivity was removed with an active charcoal filter. Behind this filter and a trap to remove fine dust particles, the main ventilator (Rietschle, type RER 47040) of the volatilization chamber was mounted. The flow volume was measured with a gas meter (RMG, type TRZ 03).

The rate of volatilization of parathion for each sampling period was calculated from the air volumes passing through the channels during each sampling period and the concentrations of parathion in these air volumes.

To enable the comparison of the results of the laboratory experiment with those of the field experiment, the sampling periods were similar in both experiments. The polyurethane foams in the cartridges were changed at 1 h 15 min, 2 h 15 min, 3 h 00 min, 5 h 25 min, 6 h 17 min, 7 h 17 min, 20 h 43 min, 21 h 43 min, 24 h 10 min and 25 h 10 min after application.

Due to a failure in the electricity supply system, the conditions in the volatilization chamber could not be regulated from 11 h to 19 h after application. During this period, there was no air flow through the chamber.

2.2.5 Extraction of polyurethane foam

Before the start of the experiment, the polyurethane foams plugs were cleaned to remove contaminants in the foam which might interfere with the analysis of the pesticides. The foams were extracted, first with toluene and then with acetone, at 120 °C using the procedure of Niehaus et al. (1990). The foams were dried in an oven (Memmert, type UL 50) at 20 °C.

After sampling the air, each foam was transferred into a glass extraction vessel (Niehaus et al., 1990) and about 350 mL acetone (technical grade) was added. Each foam was extracted at room temperature by compressing the foam with a glass weight and subsequent decompression, which was repeated 19 times. The acetone was transferred into a glass flask by opening a valve at the bottom of the extraction vessel. Then, the extraction was repeated four times with 250 mL acetone (technical grade). The extracts of each foam were collected in the same flask. The mass of the combined extract for each foam was weighed. A volume of 5 mL subsample from each extract was put into 20 mL vials. After the addition of 10 mL Ultima Gold XR (Packard) as scintillator, the vials were placed in a liquid scintillation analyzer (Packard 2550 TR/LL). The radio-activitity in each solution was measured by counting the number of desintegrations during 10 min. The limit of determination of labeled parathion in the extracts was 1.7 Bq. From the radioactivity measured in each vial, the total radioactivity in each extract was calculated.

At the end of the first nine sampling periods, only the first of the three polyurethane foams placed in series in both channels was changed and extracted with acetone. At the end of the experiment (25 h 10 min after application) all three polyurethane foams of both channels were extracted. No radioactivity was measured on the second and third polyurethane foams of both channels.

2.2.6 Measurement of the mass balance of parathion

At the end of the experiment, additional measurements were done to quantify the terms contributing to the mass balance of parathion. For the measurement of the fraction of radioactivity remaining on the plant surfaces, the plants were cut just above the soil surface and transferred into 1.8 L extraction vessels. About 750 mL acetone (technical grade) was added to each vessel and the plant material was homogenized with a mixer (Süd-Laborbedarf, type Omni 17106) for about 1 min.

The supernatant was collected by filtration of the combined mixture with a filter (Schleicher & Schuell, 185 mm diam.). To avoid quenching caused by the colour of the extract, a 1 mL sample of the extract was diluted 44 times. Two samples of 5 mL each were taken from the diluted extract and transferred into 20 mL vials. A volume of 10 mL of Ultima Gold XR (Packard) was added to each vial as scintillator. The radioactivity in the samples was measured with a liquid scintillation analyzer.

For the determination of the radioactivity remaining in the plant material, the residue remaining on the filter was dried in an oven (Memmert, type UL 40) for about 24 h at 20 °C. The dried residues were weighed and partitioned over four 250-mL beakers of a grinding apparatus (Retsch, type Planeten-Schnellmühle PM-4), each of which contained 4 Achat balls (diam. 30 mm). After grinding for about 7 min at a rate of 1200 cycles per min, the residues were combined again and mixed manually for about 1 min. Thereafter, six pellets of about 0.3 g each were pressed with a manual pressing apparatus (Parr Instruments). Each pellet was combusted in a sample oxidizer (Packard Tec., type 307). The $^{14}CO_2$ released was trapped in Carbosorb (Canberra-Packard), which was mixed with permafluor (Canberra-Packard) as scintillator. After these samples had cooled down to room temperature, the radioactivity in each sample was measured with a liquid scintillation analyzer.

The volumes of condensation water collected in the cooling traps were combined and two samples of 5 mL each were transferred into 20 mL vials. After addition of 10 mL Ultima Gold XR (Packard) as scintillator, the radioactivity in each sample was measured with a liquid scintillation analyzer.

The radioactivity collected in the CO_2 traps was determined by transferring a 10 mL sample of the liquid in each cylinder into two vials. After addition of Ultima Gold XR (Packard) as scintillator, the radioactivity in each sample was measured with a liquid scintillation analyzer.

The walls of the volatilization chamber and the edge of the experimental platform were decontaminated with paper tissues, which had been dipped in acetone. These tissues were pressed into pellets and fully combusted in an oxidizer (Packard Tec., type 307). The $^{14}CO_2$ released was trapped in Carbosorb (Canberra-Packard), which was subsequently mixed with permafluor (Canberra-Packard) as scintillator. After cooling the sample to room temperature, its radioactivity was measured with a liquid scintillation analyzer.

2.2.7 Identification of compounds in foam and plant extracts

At the end of the first, fourth and tenth air sampling period, thin-layer chromatograms were made for the extracts of the first foam plugs of the upper air channel. The procedure for this analysis was the same as that described in Section 2.2.2.

At the end of the experiment, a check was made on the formation of metabolites from parathion on plant material. A sample from the plant extract was analysed by thin-layer chromatography (See Section 2.2.2).

3 Results

3.1 Field experiment

3.1.1 Weather conditions

The course with time of the hourly average air temperature at a height of 0.8 m above the ground is presented in Figure 5A. On the day of application, the air temperature ranged from about 8 °C early morning to about 21 °C in the afternoon. On the next day, the range of air temperatures was similar, but thereafter the daily amplitude of the air temperature became smaller. At the end of the first week after application the maximum temperature reached during the day was lower than during the first two days after application.

The course with time of the hourly average net radiation is presented in Figure 5B. This course roughly corresponds to that for the average hourly air temperature. On the day of application and on the following day, the net radiation reached comparatively high values: about 420 W m^{-2}. On later days, net radiation did not exceed 350 W m^{-2}, whereas on the second and fourth days, hourly net radiation ranged up to only about 150 W m^{-2}.

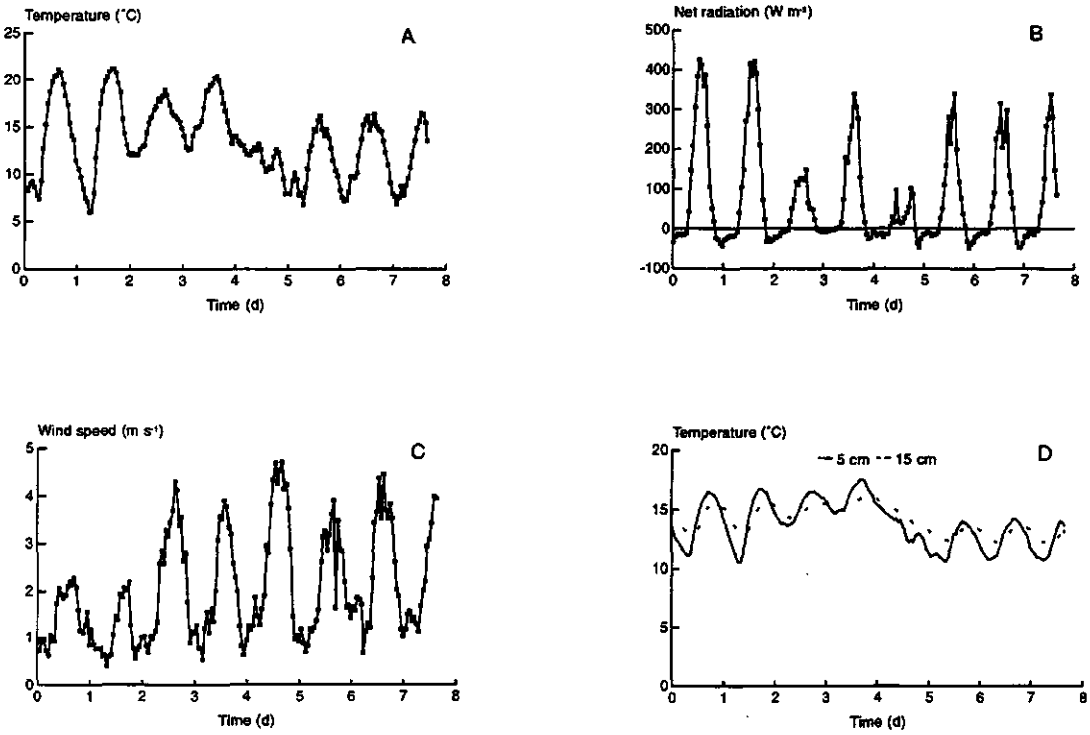

Fig. 5 Hourly average air temperature at 0.8 m above the ground (A), net radiation at 1.5 m above the ground (B), wind speed at 2 m above the ground (C) and soil temperature at depths of 0.05 and 0.15 m (D) at the Biddinghuizen field. Zero time = August 18, 1993, 0.00 h (Central European Summer Time)

Hourly data on the wind speed at a height of 2.0 m above the ground are presented in Figure 5C. On the day of application and on the day thereafter, the hourly average wind speed was rather low, between 0.4 and 2.2 m s^{-1}. From the second to the seventh day after the day of application, hourly wind speeds were higher: they ranged up to about 5 m s^{-1}. During the first week after application, wind speeds decreased to about 1 m s^{-1} in the course of the evening.

The course of the hourly average temperature of the soil at depths of 0.05 and 0.15 m are given in Figure 5D. As expected, the daily amplitude of the soil temperature at a depth of 0.15 m was lower than that at a depth of 0.05 m. During the second half of the first week after the application, the average soil temperature was somewhat lower than that during the first half of this week.

Data on the daily and the cumulative rainfall are given in Figure 6. During the first three days after the day of application, the weather was mostly dry. On the fourth day after the day of application 19.1 mm of rain fell, but on the following days only small amounts of rain fell (a few mm). As expected, net radiation was comparatively low during periods with rainfall (See Figure 5B).

During the day of application, the wind direction was predominantly north-northeast. During the next morning, the wind direction shifted towards west-northwest and this direction prevailed during the whole remaining period (up to the seventh day after the day of application) in which air samples were taken.

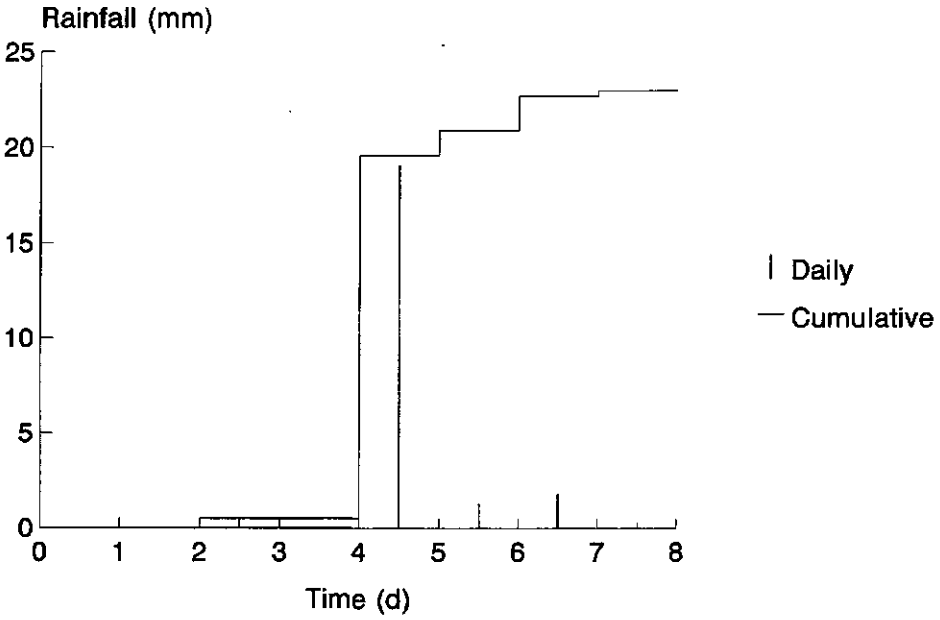

Fig. 6 Daily (bars) and cumulative rainfall (solid line) at the Biddinghuizen field. Zero time = August 18, 1993, 0.00 h (Central European Summer Time)

3.1.2 Fate of parathion

3.1.2.1 Rate of decline on potato leaves

The course with time of the fraction of the dosage of parathion remaining on the potato leaves is given in Figure 7. During the first few hours after application, there was a strong decrease in the fraction remaining: a loss of 51% of the dosage of parathion occurred in four hours. Thereafter, the decrease was more gradual. At about 7 d after application, only 0.6% of the dosage remained. More detailed data on the areic mass of parathion on the leaves after application to a potato crop are given in Annex 2.

3.1.2.2 Rate of volatilization

The rates of volatilization of parathion from the potato crop as determined with the aerodynamic (AD) and Bowen-ratio (BR) methods are presented in Table 2. As expected, the volatilization rates were highest shortly after application. At 1.6 h after application the rate of volatilization of parathion as determined with the AD method was 1 400 μg m^{-2} h^{-1} and it decreased to 245 μg m^{-2} h^{-1} at 6.6 h after application. The corresponding volatilization rates as determined with the BR method were 2 620 and 212 μg m^{-2} h^{-1}. This decrease can largely be explained from the decrease in the

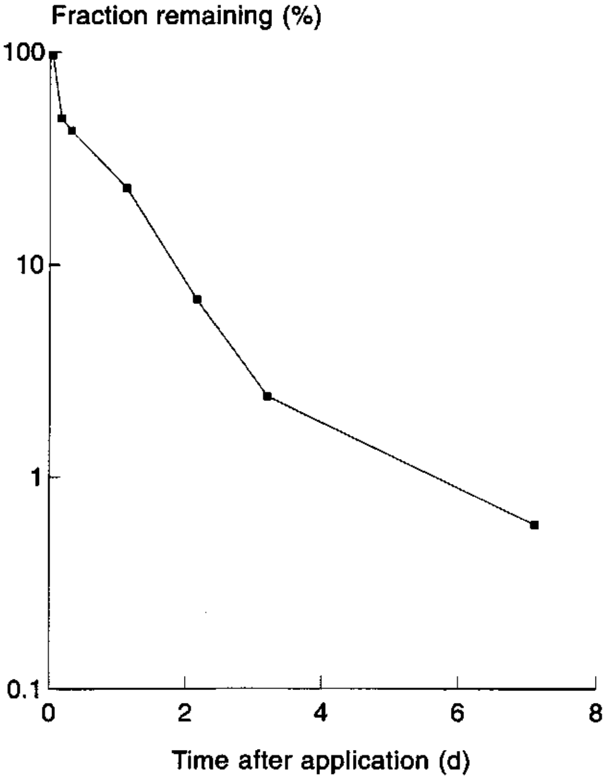

Fig. 7 Fraction of the dosage of parathion remaining on top leaves of the potato crop at the Biddinghuizen field

Table 2 The flux density of the emission of parathion into the air determined with the aerodynamic (AD) and Bowen ratio (BR) methods during the first week after application to a potato crop. Day and time of application: August 18, 1993, 12.36 - 12.55 h (Central European Summer Time)

Date	Period (h)	Time after application (d)	Flux density (μg m^{-2} h^{-1})	
			AD method	BR method
August 18	13.53 - 14.53	0.07	1 400	2 620
August 18	15.38 - 16.38	0.14	1 130	1 960
August 18	17.02 - 18.02	0.20	655	696
August 18	18.54 - 19.54	0.28	245	212
August 19	9.20 - 10.20	0.88	--[a]	--[b]
August 19	12.45 - 13.45	1.02	633	1 290
August 19	16.00 - 17.00	1.16	668	1 180
August 19	17.10 - 18.10	1.21	351	594
August 20	13.40 - 14.40	2.06	425	633
August 20	15.00 - 16.00	2.12	452	835
August 21	15.00 - 16.00	3.12	90	178
August 21	16.14 - 17.14	3.16	52	111
August 25	10.53 - 12.53	6.96	7	11
August 25	13.05 - 15.05	7.05	19	22

[a] zero wind speed gradient

[b] zero water vapour pressure gradient

concentration gradient and the wind speed gradient and from the less unstable atmospheric conditions. Later in the afternoon, the ambient temperature decreased which probably contributed to the decrease in the volatilization rate. The decrease in temperature corresponds with that in net radiation (See Annex 3, Tables A3.2 and A3.4).

At 1.0 d after application, the rate of volatilization of parathion determined with the AD method was 633 μg m^{-2} h^{-1}. Because of a variable wind direction, the measurement site for the pesticide concentration gradient was situated upwind of the treated field during part of the sampling period. Therefore, the volatilization rate was probably higher than that determined. About three hours later, the volatilization rate was not much different: 668 μg m^{-2} h^{-1}. At that time, the wind direction was fairly constant (ranging from 260 to 340°) and during the whole sampling period the measurement site was downwind. Later, at 1.2 d after application, the volatilization rate had decreased to 351 μg m^{-2} h^{-1}, which can be explained from the lower pesticide concentration and lower wind speed gradients.

The volatilization may have been reduced by the lower ambient air temperatures (at 0.8 m above the ground), although this decrease was comparatively small, i.e. 0.5 °C. Presumably, the decrease in the fraction of parathion remaining on the plant leaves has also contributed to the decrease in the volatilization rate (See Figure 7). On this day, the rates of volatilization determined with the BR method were higher than those determined with the AD method: they ranged from 1290 μg m^{-2} h^{-1} for the first period to 594 μg m^{-2} h^{-1} for the last period.

At 2.1 d after application, the rate of volatilization of parathion determined with the AD method ranged from 425 to 452 μg m^{-2} h^{-1}. The greater wind speed gradient measured above the crop as compared to that for the day before (See Annex 3, Table A3.4) would be expected to promote the rate of volatilization. However, this effect is diminished by that of a decrease of about 2 °C in ambient air temperature (at 0.8 m above the ground), which lowers the rate of volatilization. The decrease in air temperature corresponds with a decrease in net radiation: from 348 to 128 W m^{-2} (See Annex 3, Table A3.2). On this day, the percentage of the dosage of parathion measured on the plant leaves was substantially lower than that measured on the day before: 7 vs. 23%. This decrease will also have contributed to the lower estimated volatilization rate as compared to that estimated for the second and third series of the day before. The corresponding rates as determined with the BR method were 1.5 to 1.8 times those determined with the AD method.

At 3.1 d after application, the rate of volatilization determined with the AD method was substantially lower than that measured on the day before: 90 μg m^{-2} h^{-1} vs. 452 μg m^{-2} h^{-1}. This is due to the decrease in the concentration gradient above the crop, which was about one-fourth of that measured at 2.1 days after application. About 1.2 h later (around 17.00 h), the volatilization rate was only 52 μg m^{-2} h^{-1}, which can be explained from the lower wind speed and concentration gradients. It can be expected that the decrease in ambient temperature (about 0.5 °C) and the decrease in the fraction of parathion remaining on the plant leaves contributed to this effect. The rate of volatilization as determined with the BR method for the first period was about two times that determined with the AD method. The subsequent decrease in the volatilization rate was similar to that determined with the AD method.

At 7.0 d after application, the rate of volatilization of parathion determined with the AD method decreased further to 7.0 μg m^{-2} h^{-1} for the first measuring period and 19 μg m^{-2} h^{-1} for the second measuring period. On this day, the concentration gradients measured were about 0.12 times those measured on the third day after the day of application. This can largely be explained by the decrease in ambient temperature (about 5°) and the decrease in the fraction of parathion remaining on the plant leaves. At this day, the rates of volatilization as determined with the BR method were about the same as those determined with the AD method.

The rates of volatilization of parathion determined with the AD and BR methods, expressed as a percentage of its dosage, are presented in Figure 8. For most sampling periods, the rate of volatilization of parathion as determined with the AD method was lower than that determined with the BR method. The average ratio between the rate determined with the AD method and that determined with the BR method was 0.63 (95% confidence interval from 0.54 to 0.74). The difference between the volatilization rates as determined with the two methods is significant.

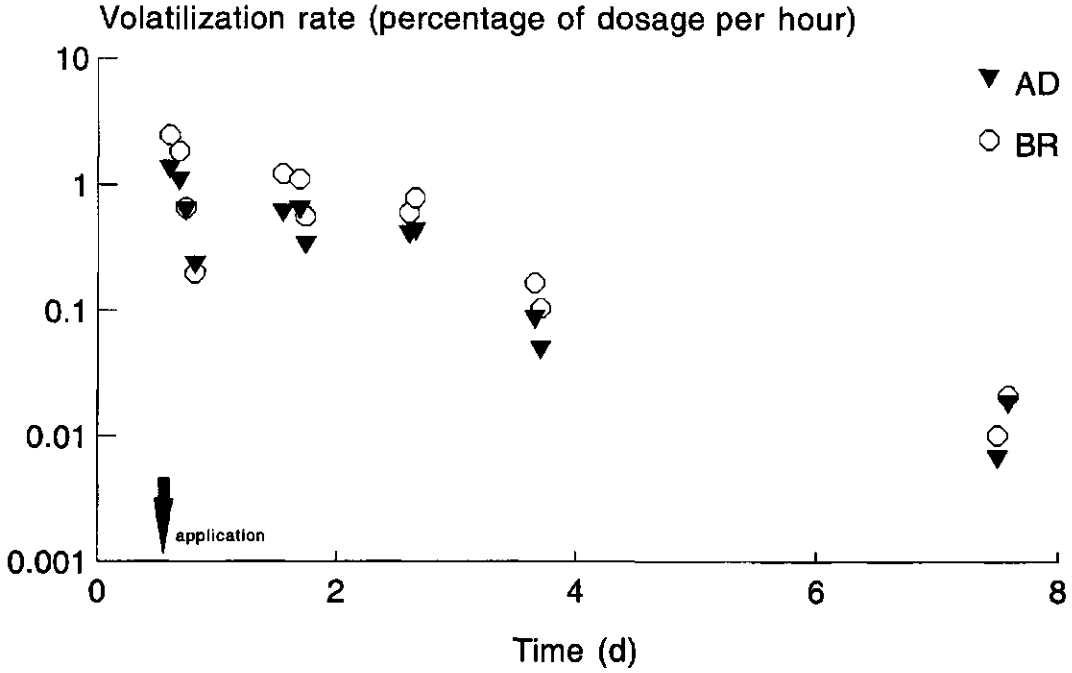

Fig. 8 Hourly flux density of the emission of parathion from a potato crop into the air. Determined with aerodynamic (AD) and Bowen-ratio (BR) methods. Zero time = August 18, 1993, 0.00 h (Central European Summer Time). Dosage of parathion = 1.06 kg ha^{-1}

During the seventh hour after the application of parathion, the volatilization rate was about 0.1 times that determined during the first hour. Presumably, this is mainly due to the course with time of meteorological factors influencing the volatilization rate, such as temperature, wind speed and stability of the surface air layer. The rate of decline of parathion on the potato leaves was substantial, but at eight hours after application still 43% of the dosage remained (See Figure 7). From the first to the 7th day after the day of application, the decrease of the daily average rate of volatilization of parathion roughly follows that of the rate of decline of its fraction remaining on the potato leaves. A smaller fraction of parathion remaining on the potato leaves can be expected to result in smaller concentration gradients in the air layer above the potato crop and consequently in lower volatilization rates as determined with the AD and BR methods.

3.1.3 Fate of chlorothalonil

3.1.3.1 Rate of decline on potato leaves

The course with time of the fraction of the dosage of chlorothalonil remaining on the potato leaves is given in Figure 9. During the first week after application, there was no distinct decrease in the fraction of the dosage remaining on the plant leaves. More detailed data on the areic mass of chlorothalonil on the leaves after application to a potato crop are given in Annex 2.

3.1.3.2 Rate of volatilization

The rates of volatilization of chlorothalonil from the potato crop as determined with the AD and BR methods are presented in Table 3. Shortly after spraying, the rate of volatilization of chlorothalonil determined with the AD method ranged from 59 to 66 μg m^{-2} h^{-1}. Later on the day the volatilization rate decreased to 12 μg m^{-2} h^{-1}. Similar to the decrease in the volatilization of parathion, this decrease can be ascribed to a less unstable atmosphere and lower concentration and wind speed gradients. Presumably, the decrease in ambient temperature has substantially contributed to the lower concentration gradient of chlorothalonil above the crop surface.

At 1.0 d after application, the rate of volatilization of chlorothalonil determined with the AD method was 75 μg m^{-2} h^{-1}. However, because of a changing wind direction, the measurement site was upwind during part of the sampling period, which probably resulted in under-estimation of the volatilization rate of chlorothalonil. About three hours later, the volatilization rate was estimated to be 103 μg m^{-2} h^{-1}. Thereafter, at 1.2 d after application, the volatilization rate decreased to 60 μg m^{-2} h^{-1}. Similar to parathion, this decrease in the volatilization rate can be explained from the lower wind speed gradient and the smaller pesticide concentration gradient (See Annex 3, Tables 3 and 4). On average, the rate of volatilization determined with the BR method was 1.8 times that calculated with the AD method.

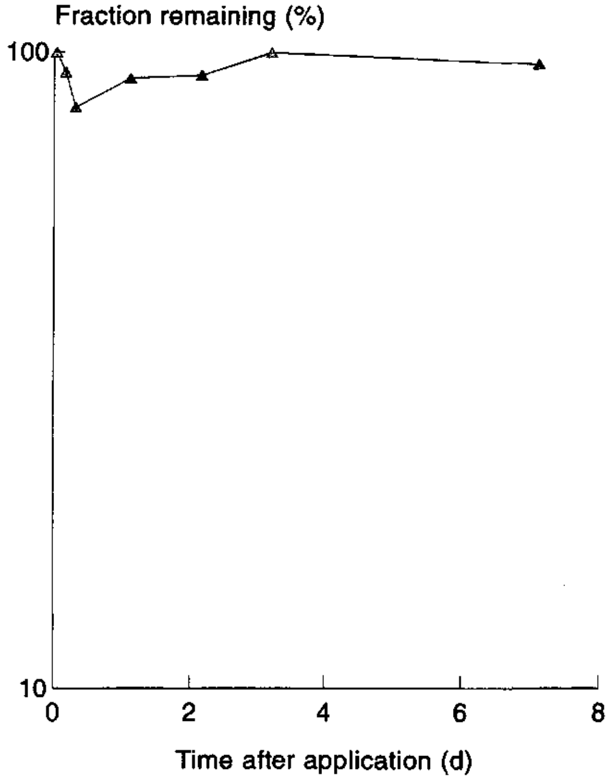

Fig. 9 Fraction of the dosage of chlorothalonil remaining on top leaves of the potato crop of the Biddinghuizen field

Table 3 The flux density of the emission of chlorothalonil into the air determined with the aerodynamic (AD) and the Bowen ratio (BR) methods during the first week after application to a potato crop. Day and time of application: August 18, 1993, 12.36 - 12.55 h (Central European Summer Time)

Date	Period (h)	Time after application (d)	Flux density ($\mu g\ m^{-2}\ h^{-1}$) AD method	Flux density ($\mu g\ m^{-2}\ h^{-1}$) BR method
August 18	13.53 - 14.53	0.07	59	110
August 18	15.38 - 16.38	0.14	66	114
August 18	17.02 - 18.02	0.20	50	54
August 18	18.54 - 19.54	0.28	12	10
August 19	9.20 - 10.20	0.88	--[a]	--[b]
August 19	12.45 - 13.45	1.02	75	153
August 19	16.00 - 17.00	1.16	103	182
August 19	17.10 - 18.10	1.21	60	102
August 20	13.40 - 14.40	2.06	76	114
August 20	15.00 - 16.00	2.12	86	159
August 21	15.00 - 16.00	3.12	83	164
August 21	16.14 - 17.14	3.16	58	125
August 25	10.53 - 12.53	6.96	44	67
August 25	13.05 - 15.05	7.05	43	49

[a] zero wind speed gradient
[b] zero water vapour pressure gradient

At 2.1 d after application, the rates of volatilization of chlorothalonil determined with the AD method were not much different from those estimated for the first day after the day of application: they were 76 and 86 $\mu g\ m^{-2}\ h^{-1}$. Although the concentration gradient in air was substantially lower than that measured at 1.1 d after application, the higher wind speed gradient resulted in a similar volatilization rate as that determined on the day before. At this time, the average volatilization rate as determined with the BR method was 1.7 times that determined with the AD method.

At 3.1 d after application, the rate of volatilization determined with the AD method was 83 $\mu g\ m^{-2}\ h^{-1}$. This volatilization rate did not differ much from those determined one day earlier. Although the concentration gradient measured in air was somewhat higher than those measured on the day before, its effect on the volatilization rate was counter-balanced by a lower wind speed gradient. About 1.2 h later, a somewhat lower volatilization rate was determined: 58 $\mu g\ m^{-2}\ h^{-1}$. This decrease is mainly due to a combined effect of lower wind speed and smaller pesticide concentration gradient. For the measurements of this day, the rate of volatilization as determined with the BR method was 2.1 times that determined with the AD method.

At 7.0 d after application, the rates of volatilization of chlorothalonil determined with the AD method were almost the same for both periods, i.e. 43 $\mu g\ m^{-2}\ h^{-1}$. These rates were on average 0.6 times those determined at 3.1 days after application. Presumably, this has been caused by the lower ambient air temperature as measured at 0.8 m above the ground: 16 vs. 20 °C (See Annex 3, Table A3.4). The volatilization rates as determined with the BR method were on average 1.3 times those determined with the AD method.

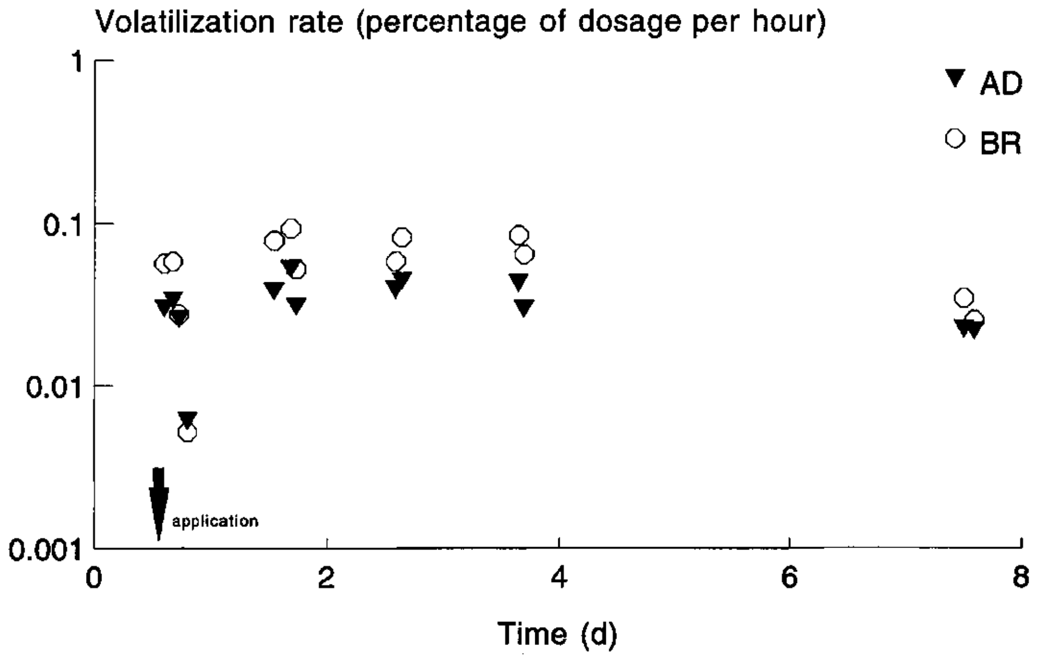

Fig. 10 Hourly flux density of the emission of chlorothalonil from a potato crop into the air. Determined with aerodynamic (AD) and Bowen-ratio (BR) methods. Zero time = August 18, 1993, 0.00 h (Central European Summer Time). Dosage of chlorothalonil = 1.94 kg ha^{-1}

During the first week after application, the rates of volatilization determined with the AD method were mostly of the same order of magnitude: between about 45 and 100 µg m^{-2} h^{-1} (i.e. a few hundredths percent of the dosage per hour). The volatilization rates measured shortly after application were not much higher than those determined at 7 d after the application, which indicates a comparatively high persistence of this pesticide on the potato leaves. This is confirmed by the finding that there was no distinct decrease in the fraction of the dosage remaining on the plant leaves during the first week after application (See Section 3.1.3.1).

The rates of volatilization of chlorothalonil determined with the AD and BR methods, expressed as a percentage of its dosage, are presented in Figure 10. The difference between the volatilization rate determined with the AD method and that determined with the BR method is similar to that for parathion and it is significant (P-value < 0.001).

3.2 Laboratory experiment

3.2.1 Simulation of field conditions

The data on the air temperature as measured during the experiment in the volatilization chamber and those measured during the corresponding time interval at about 0.3 m above the crop in the field are presented in Figure 11. In this figure, the data for the temperature program of the experiment in the volatilization chamber are also given. The course with time of the air temperature as programmed for the experiment corresponded closely to that in the field. During the first five hours of

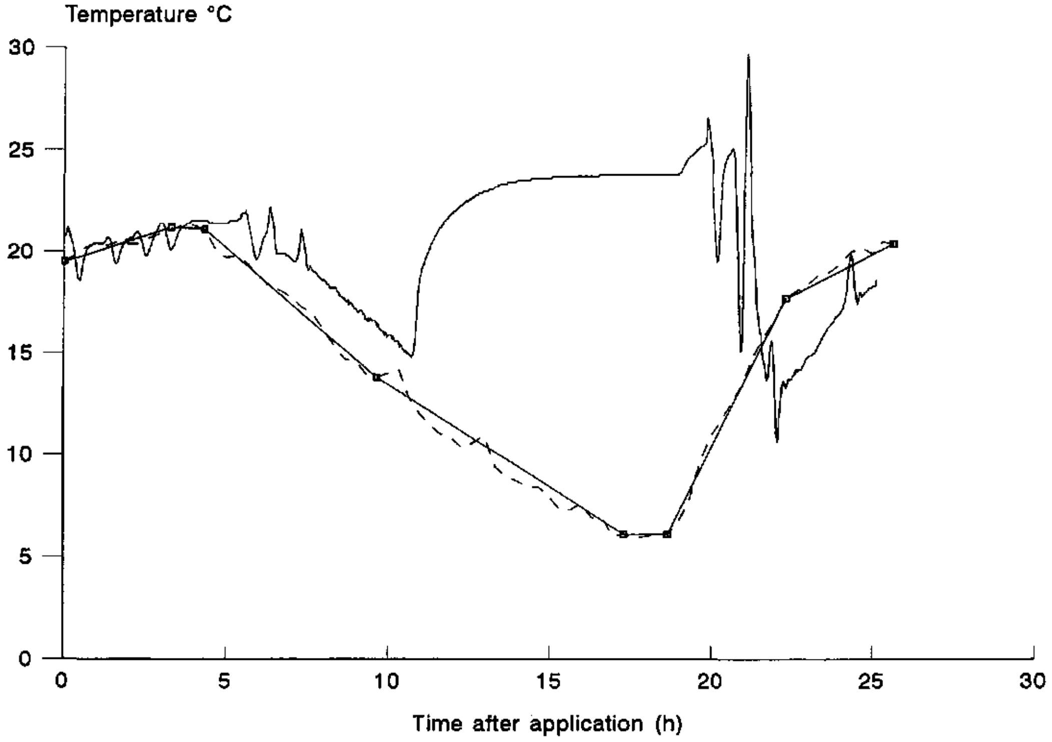

Fig. 11 Air temperature as measured in the field (- -) and in the volatilization chamber (——) during the first day after spraying. ■——■ = temperature programmed for the chamber

the experiment, the air temperature in the volatilization chamber corresponded well with that measured in the field. For the next six hours, the temperature measured in the volatilization chamber was about 2 °C higher than that measured in the field. At about 11 h after application, the air temperature in the volatilization chamber started to increase instead of further decreasing due to a failing electricity system. At 19 h after application, the electricity system started functioning again and consequently the difference between the temperature in the volatilization chamber and that in the field decreased. During the last few hours, the temperature in the chamber was on average about 2 °C lower than that in the field.

The data on the relative air humidity as measured during the experiment in the volatilization chamber and those measured during the corresponding time interval at about 0.3 m above the crop in the field are presented in Figure 12. In this figure, the data for the air humidity program of the experiment in the volatilization chamber are also given. The course with time of the relative air humidity in the volatilization chamber as programmed for the experiment corresponded well with that measured in the field. However, the actual course with time of the relative humidity in the volatilization chamber was different from that measured in the field. During the first three hours, the relative humidity in the field changed only slightly, whereas in the volatilization chamber the variation in the relative air humidity was about 20%. During the next five hours, the air humidity increased both in the field and in the volatilization chamber, but the relative humidity as measured in the chamber was somewhat higher than that prevailing in the field. In the period in which the control system did not function, the relative humidity in the chamber was roughly 20% lower than that prevailing in the field. After the system started functioning again, there

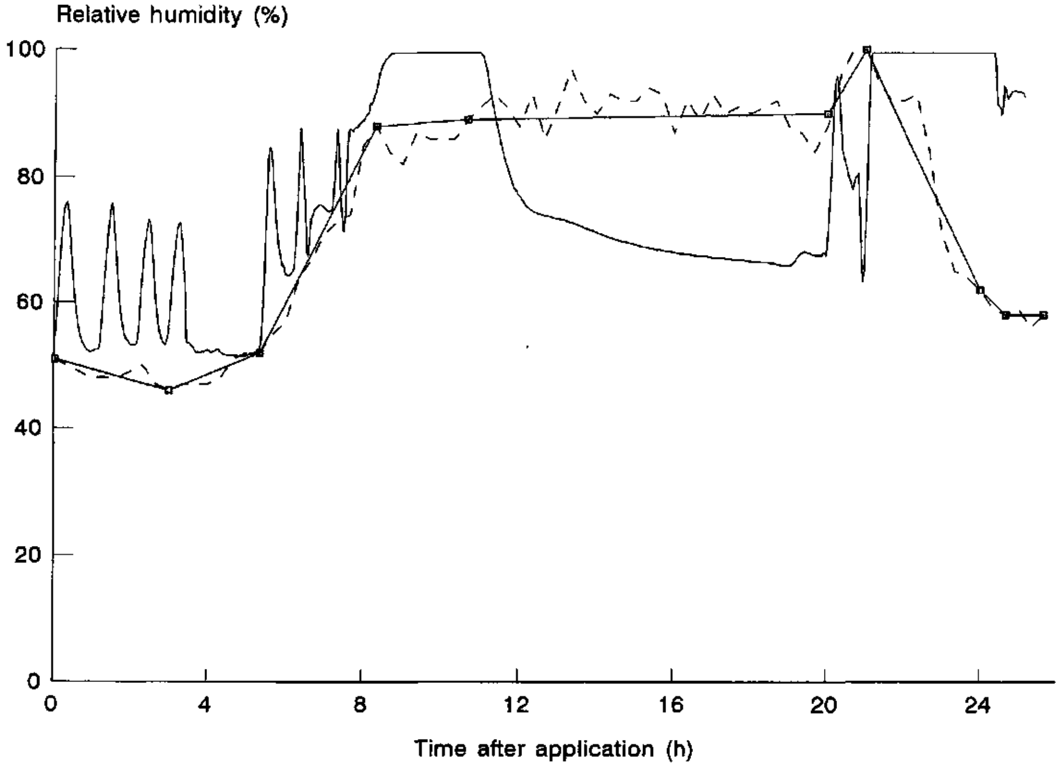

Fig. 12 Relative air humidity (RH) as measured in the field (- -) and in the volatilization chamber (——) during the first day after spraying. ■——■ = RH programmed for the chamber

remained a substantial difference between the relative air humidity in the volatilization chamber and that measured in the field.

The data on the wind speed above the plant stand in the volatilization chamber during the experiment and those measured at crop height in the field during the first 24 h after application are presented in Figure 13. In this figure, the data for the wind speed program of the experiment in the volatilization chamber are also given. There was a distinct difference between the programmed course with time of the wind speed in the volatilization chamber and that measured in the field. This is mainly due to the fact that the 10-min average values for the wind speed as measured in the field were taken for 20-min average values. However, during the first seven hours after application, the average wind speed in the volatilization chamber corresponded to that measured in the field. For the period between 7 and 11 h after application, there was a substantial difference in the wind speed in the volatilization chamber and that prevailing in the field: it ranged up to about 0.6 m s^{-1}. Due to the failing electricity supply, there was no wind in the volatilization chamber between 11 and 19 h after application. Between 19 and 22 h after application, the wind speed in the volatilization chamber increased to about 1.2 m s^{-1} and subsequently decreased again to 0.5 m s^{-1}, whereas the wind speed in the field remained comparatively low, i.e. about 0.4 m s^{-1}. During the remaining three hours of the experiment, the wind speed in the chamber remained constant and that in the field increased to about 1.1 m s^{-1}.

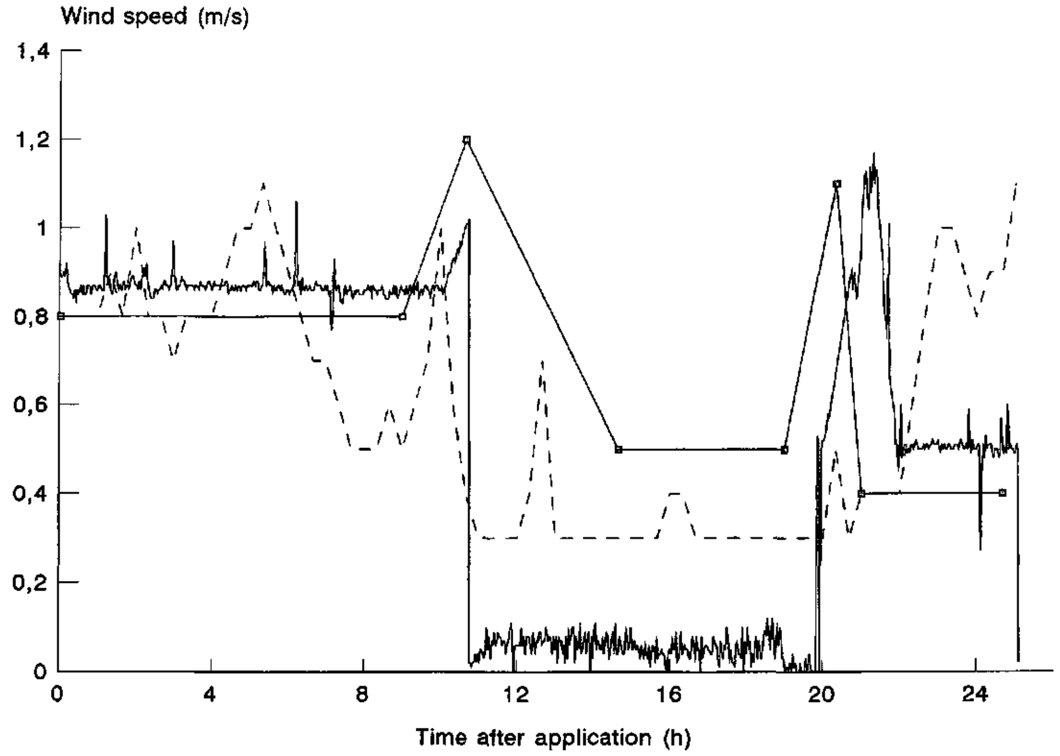

Fig. 13 Wind speed at crop height as measured in the field (- -) and that above the plant stand in the volatilization chamber (—) during the first day after spraying. ■—■ = wind speed programmed for chamber

3.2.2 Fate of parathion

The course with time of the rate of volatilization of parathion from the potato plants, expressed as a percentage of its dosage, is presented in Figure 14. During the first six hours, there was a distinct increase in the hourly rate of volatilization. The maximum hourly volatilization rate was measured to be 2.2% of the dosage and it occurred between 5.4 and 6.3 h after application. During the next hour, the hourly volatilization was lower, i.e. 1.7% of the dosage. This initial course with time of the volatilization rate may be largely due to the course with time of the air temperature. During the first six hours, there was a gradual increase in the air temperature, but thereafter it decreased (See Fig. 11).

During the period from 11 to 19 h after application, the climate conditioning system and the air sampling system of the volatilization chamber did not function. During this time, there was no wind in the volatilization chamber. Consequently, the hourly volatilization rate of parathion in this period was comparatively low.

At 21.2 h after application, a comparatively high hourly volatilization rate was measured. During the next few hours, the volatilization rate decreased substantially. This can be explained by a comparatively low air temperature, i.e. about 14 °C at 23 h after application, whereas during the previous measurement the air temperature rose to 29 °C. At 24.7 h after application, the rate of volatilization of parathion increased again. This may be due to the increase in the air temperature from about 14 to 18 °C.

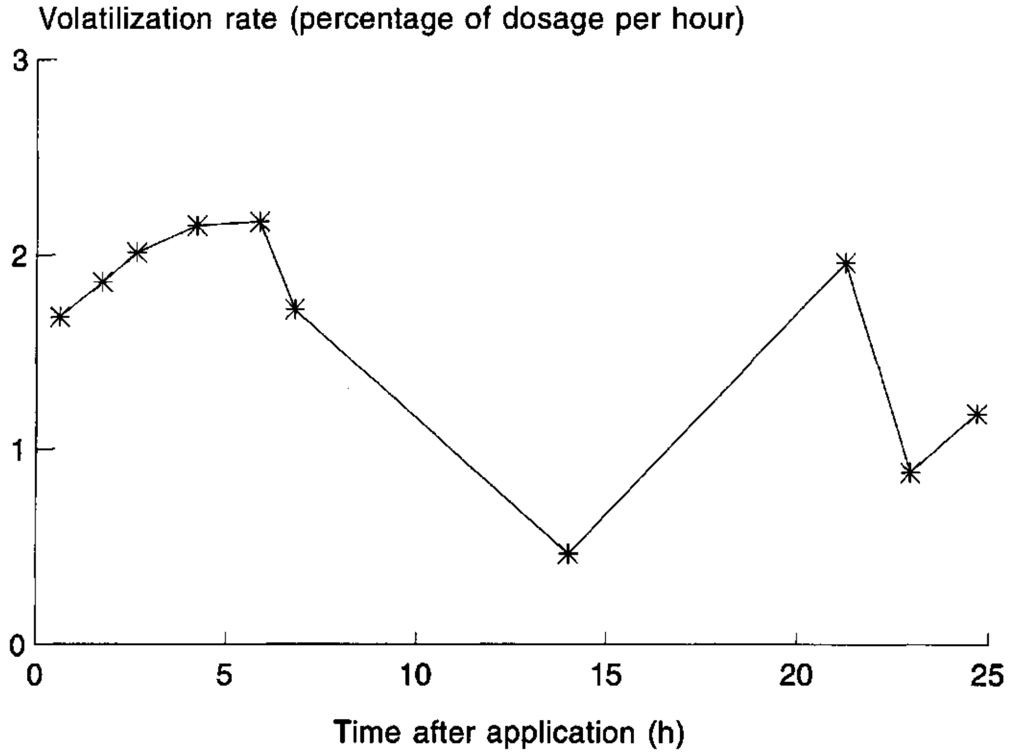

Fig. 14 Hourly volatilization of parathion from potato plants measured in the SLFA volatilization chamber with simulation of the conditions prevailing during the Biddinghuizen field experiment

More detailed information on the mass of parathion volatilized during each sampling period is given in Annex 4, Table A4.1.

The ratio between the ^{14}C-labeled parathion in the samples taken from the outgoing air of the lower channel and that in the samples taken from the outgoing air of the upper channel was rather constant, i.e. 0.41 (n = 10, s.d. = 0.04; See Annex 4, Table A4.2). The larger fraction of parathion as measured in the air from the upper channel can be explained by the higher wind speed of the air layer above the crop compared with that of the air layer within the crop.

The thin-layer chromatograms of the extracts of the polyurethane foams showed that almost all the radioactivity was caused by parathion, so no other volatile metabolites were formed in substantial amounts during the experiment.

3.2.3 Mass balance of parathion

The results of the measurements to quantify the terms of the mass balance of parathion at the end of the experiment are given in Table 4. The total mass of parathion volatilized was measured to be 4.72 mg, which corresponds to 25.8% of the dosage.

Table 4 Terms of the mass balance of parathion at the end of the experiment

Surface or material	Radioactivity (kBq)	Mass collected (mg)	Percentage of dosage[a] (%)
PU-foams	160.51	4.72	25.8
cooling traps	0.00	0.00	0.0
CO_2 traps	0.00	0.00	0.0
Plants	352.13	10.34	56.6
Non-extractable[b]	74.51	2.19	12.0
Platform	2.39	0.07	0.4
Chamber walls	0.67	0.02	0.1

[a]Radioactivity applied to the plants is set at 100% (621.73 kBq); [b] Plant residues.

Decontamination of the volatilization chamber resulted in a recovery of 0.67 kBq or 0.02 mg parathion. This is much less than the mass of parathion collected on the polyurethane foams, i.e. 4.72 mg, so adsorption of parathion from the gas phase onto the walls of the volatilization chamber was minimal.

At the end of the experiment, most of the radioactivity applied still remained on the plants, i.e. 68.6%. The thin-layer chromatogram of the combined extracts of the plants showed that the radioactivity originated predominantly from parathion. No major metabolites were detected in the chromatogram.

The total radioactivity accounted for was 590.21 kBq, which corresponds to 94.9% of the dosage of parathion applied to the plants.

4 Discussion and conclusions

As expected, the highest volatilization rates were determined shortly after application. The volatilization rate of parathion ranged up to a few percent of its dosage per hour. During the first seven hours there was a strong decrease in the volatilization rate. No measurements for determining the volatilization rate were made during the first hour after application; a substantial fraction of the dosage of parathion may have been lost by volatilization during that period.

At the end of the first week after the application of parathion, its volatilization rate had decreased to about one hundredth percent of the dosage per hour. This low volatilization rate corresponded with the low fraction of parathion remaining on the potato leaves as measured shortly after the end of the last sampling period, i.e. less than 1% of its dosage. Therefore, no substantial loss of parathion by volatilization is likely to occur following the first week after its application to a potato crop.

An estimate of the cumulative volatilization can be made using average values for the volatilization rate each day. It is assumed that volatilization only occurs between sunrise and sunset. Because there was a sharp decrease in the rate of volatilization during the first eight hours after application, average values of the rate of volatilization were taken for the first and the second four-hour period. For the period between the third and seventh days after the day of application, average values for the volatilization rate were obtained by linear interpolation of the average volatilization rates as determined by the measurements on the third and seventh days. The fraction of parathion volatilized during the first day after application was calculated to be 9% of its dosage. For the first week after application, the cumulative volatilization was calculated to be about 30% of the dosage. Because hardly any parathion was measured to remain on the leaves at one week after application, hardly any further increase in the cumulative volatilization could occur. Probably, the largest fraction of the dosage was transformed. However, a fraction of the mass of parathion in the plant leaves may not have been extracted with the method used resulting in an under-estimation of the fraction of parathion remaining. The rate of volatilization of this fraction may be extremely low.

During the first week after the application of chlorothalonil, there was not a great change in its volatilization rate. The rate was around a few hundredths percent of the dosage per hour. The cumulative volatilization of chlorothalonil was estimated in a similar way as that for parathion. During the first day after application, the cumulative volatilization of chlorothalonil was calculated to be 0.6%. For the first week after application, the cumulative loss of chlorothalonil by volatilization was estimated to be 4.9% of its dosage.

The fraction of chlorothalonil remaining on the plant leaves hardly decreased during the first week after application. Therefore, it can be expected that the volatilization of chlorothalonil continues for a prolonged period after its application.

On average, the volatilization rate as determined with the AD method was about 0.6 times that determined with the BR method. It is not clear what caused this difference. Majewski et al. (1990) found no significant difference when estimating the volatilization rate of diazinon, chlorpyrifos, lindane and nitrapyrin from a bare soil using the AD and BR methods. However, for about one third of their 13 sampling periods, no data were obtained with the BR method, so only a limited comparison could be made. Further, for some periods higher volatilization rates were determined with the BR method, whereas for other periods higher rates were determined with the AD method. The difference in volatilization rate as determined with the two methods could be related to differences in the atmospheric conditions. For example, some (n=3) of the rates determined by Majewski et al. (1990), which were highest for the AD method, were determined during periods with fairly high wind speeds, i.e. greater than 4 m s^{-1} at a height of 1.0 m. In our study, the wind speed as measured during the sampling periods at a comparable height (at about 1 m above the displacement height) remained below that value.

It should be noted that the BR method fails when the Bowen ratio approaches -1 (resulting in K values approaching infinity). This situation occurs when the sensible heat flux is directed to the surface and its absolute value equals the latent heat flux. For the periods during which volatilization measurements were made in this study, such conditions did not occur. When water vapour pressure or air temperature gradients become small, the accuracy of the estimation of the volatilization rate with this method decreases. The same holds for the AD method under weather conditions with low wind speeds and small wind speed gradients.

The magnitude of the effect of weather conditions on the rate of volatilization may be estimated from the rates determined for chlorothalonil, because the fraction of its dosage remaining on the plant leaves hardly decreased during the first week after application. The rates ranged from about 10 to 100 μg m^{-2} h^{-1}. A strong decrease indicates substantial transformation of the pesticide on the plant leaves or uptake of the pesticide by the plant. This is confirmed by the rates determined for parathion during the first week after application, which decreased by two orders of magnitude. However, some caution is necessary as volatilization may be strongly reduced under very dry weather conditions.

In the present study, no measurements were made on the fraction of the pesticide on plant leaves available for volatilization, so the course with time of the volatilization rate can only roughly be explained from the rate of decline of pesticide as measured on the plant leaves. For improvement on the description of this course, a method needs to be developed to measure the fraction of pesticide deposited on the leaves which is available for volatilization.

In the volatilization chamber of the Staatliche Lehr- und Forschungsanstalt (SLFA) at Neustadt/W. (Germany), an experiment on the volatilization of parathion from potato plants was done under similar conditions. The meteorological conditions in the first 24 hours after the application of the pesticides onto the potato crop at Biddinghuizen were simulated in the volatilization chamber. During the first seven hours, the air temperature and the wind speed in the volatilization chamber corresponded reasonably well with those measured in the field. During this time, the difference between the relative air humidity in the chamber and that prevailing in the field was sometimes comparatively large. Presumably, the present conditioning system for the climate in the volatilization chamber has a capacity which is too limited to simulate a gradual change in the relative air humidity. Unfortunately, the control system did not function in the period from 11 to 19 h after application, because of an interruption in the supply of electricity to the institute. During the remaining period of the experiment, there were distinct differences between the course with time of the meteorological conditions in the volatilization chamber and that in the field.

During the 2nd hour after application, the volatilization rate measured for parathion in the volatilization chamber corresponded well with that measured in the field: 1.9% of the dosage per hour for both systems. During the next three hours, the hourly volatilization rate as measured in the volatilization chamber increased from 1.9 to 2.2% of the dosage. Contrastingly, the hourly volatilization rate as determined in the field decreased substantially, i.e. to 0.64% at 4.9 h after application. Possibly, the humidity of the air has affected the evaporation of parathion from the leaf surfaces. During the first four hours after application, the relative air humidity in the field was about 50% or lower, whereas the humidity of the air in the volatilization chamber was higher than that measured in the field: it ranged up to 75%. At low air humidity, plant leaves dry out more quickly than at higher air humidity, which may result in a stronger adsorption of parathion on the surface of the plant leaves.

For the period between 11 and 19 h after application, no comparison can be made because the meteorological conditions in the field were not simulated in the volatilization chamber. For the period of 22 to 25 h after applicaton, the volatilization rates measured in the chamber were similar to those measured in the field: they ranged between 0.9 and 1.2% of the dosage per hour. At 24.7 h after application, the hourly wind speed in the chamber was lower than that in the field. Further, the hourly air temperature in the chamber was about 1.2 °C lower than that measured in the field, so a lower volatilization rate in the chamber than that measured in the field could be expected. However, the rate of volatilization of parathion measured in the volatilization chamber was higher than that measured in the field. Possibly, the higher relative humidity of the air in the volatilization chamber compared to that prevailing in the field resulted in an increased wetness of the plant leaves which reduced the adsorption of parathion on the leaves. Probably, the higher fraction of the dosage of parathion remaining on the plant leaves contributed to the higher volatilization rate as measured in the volatilization chamber.

During the first day after application, the cumulative emission of parathion from potato plants as measured in the volatilization chamber was 25% of its dosage. This is distinctly higher than the corresponding loss of parathion by volatilization in the field, which was estimated to be about 9% of the dosage. During part of the experiment, the air temperature and the relative air humidity in the chamber were substantially higher than those prevailing in the field. Presumably this contributed to the larger volatilization loss as measured in the volatilization chamber.

At 1 d after application, about 69% of the dosage of parathion remained on the plants in the volatilization chamber, whereas in the field only 24% of the dosage was measured to remain. The higher rate of transformation as measured in the field may have resulted from photodegradation, because during this experiment in the chamber the duration and intensity of daylight was not simulated. Therefore, the further development of the volatilization chamber by introducing a system to simulate radiation can be expected to improve the accuracy of the estimates of the rate of volatilization of pesticide obtained with this system.

After the application of a pesticide to a crop, different processes occur which affect its fate, such as adsorption, transformation, volatilization, penetration into the leaves and subsequent transport through the plant away from the deposition site. A description of the course with time of the rate of volatilization of pesticide from a crop is complex, as the physico-chemical properties of the pesticide, the characteristics of the surface of the plant leaves as well as weather conditions need to be taken into account. No single factor predominates, which can be illustrated by the study by Krasel and Pestemer (1993), who found no straightforward relationship between some physico-chemical properties of nine pesticides, such as their vapour pressure, and their cumulative volatilization in the first 6 hours after their application to bean plants.

Only few studies have been published on the factors affecting the rate of volatilization of pesticides from plant leaves. Breeze et al. (1992) studied the effect of temperature on volatilization and uptake of 2,4-D-butyl during the first 6 hours after its application to barley in plant chambers of 53 L. The hourly volatilization rate was measured to be strongly influenced by the leaf temperature as estimated from the transpiration of the leaf and its energy balance: an increase in 5 °C (from 22 to 27 °C) resulted in an eightfold increase in the volatilization rate. Therefore, comparatively high volatilization rates in the field can be expected during hours with high solar radiation. In the present study, a higher volatilization rate was measured in the afternoon of the first day after the day of application than early in the preceding evening, when net radiation was substantially lower (See Annex 3, Table 2).

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Annex 1 Rate of release of water from nozzles of spray boom

Table A1.1 Rate of release of water from nozzles of spray boom of Douven spraying machine. Spraying pressure 260 kPa

Nozzle no	Rate of release of water (mL min^{-1})
1	978.0
2	992.5
3	1018.7
4	1025.5
5	998.6
6	1012.7
7	954.0
8	1005.0
9	990.0
10	991.9
11	986.6
12	990.0

Annex 2 Areic masses of parathion and chlorothalonil on leaves after their application to a potato crop

Table A2.1 Average areic mass of parathion on potato leaves at several time intervals after application

Time after application (d)	Areic mass (mg m^{-2})
0.0	74
0.03	71
0.16	36
0.31	32
1.1	17
2.2	5.1
3.2	1.8
7.1	0.4

Table A2.2 Average areic mass of chlorothalonil on potato leaves at several time intervals after application

Time after application (d)	Areic mass (mg m^{-2})
0.0	165
0.03	172
0.16	153
0.31	136
1.1	150
2.2	152
3.2	165
7.1	158

Annex 3 Data needed for the calculation of pesticide volatilization rates

Table A3.1. Data needed for the calculation of the soil heat flux density at the surface and for that of the Bowen ratio coefficient as used for the Bowen ratio method

Time (d)	Soil heat flux at 0.08 m depth (W m^{-2})	Δ(soil temperature) (°C)	Δ(air temperature) (°C)	Bowen ratio coefficient at surface (-)	Soil heat flux (W m^{-2})
0.60	11.26	-0.008	0.185	0.281	10.10
0.67	9.89	0.023	0.202	0.318	13.32
0.73	7.56	-0.021	0.083	0.196	4.33
0.81	6.33	-0.017	-0.047	-0.123	3.71
1.55	15.93	0.061	0.160	0.188	25.21
1.69	15.79	0.052	0.120	0.146	23.61
1.74	14.55	0.007	0.050	0.066	15.63
2.59	8.63	0.064	-0.022	-0.120	18.36
2.65	9.45	0.069	0.035	0.221	19.83
3.65	12.10	0.070	0.138	0.291	22.74
3.69	12.12	0.049	0.164	0.440	19.59
7.49	6.88	0.187	0.175	0.403	35.13
7.58	7.94	0.027	0.090	0.227	11.95

Zero time = August 18, 1993, 0.00 h (Central European Summer Time).

Table A3.2 Energy balance for the Biddinghuizen field and the dispersion coefficient for sensible heat

Time (d)	Net radiation (W m^{-2})	Soil heat flux density (W m^{-2})	Sensible heat flux density (W m^{-2})	Latent heat flux density (W m^{-2})	Dispersion coefficient (m^2 h^{-1})
0.60	358.4	10.10	76.38	271.9	612.6
0.67	334.5	13.32	77.49	243.7	568.8
0.73	105.9	4.33	16.62	84.9	297.4
0.81	23.0	3.71	-2.70	22.0	84.6
1.55	397.4	25.21	58.85	313.3	545.2
1.69	298.3	23.61	35.03	239.7	432.4
1.74	178.2	15.63	10.06	152.5	299.9
2.59	108.3	18.36	-12.21	102.2	812.1
2.65	147.8	19.83	23.20	104.8	994.1
3.65	304.5	22.74	63.45	218.3	682.8
3.69	269.5	19.59	76.42	173.5	694.1
7.49	312.3	35.13	79.53	197.6	673.7
7.58	214.1	11.95	37.39	164.7	617.1

Zero time = August 18, 1993, 0.00 h (Central European Summer Time).

Table A3.3 Measured difference in concentration of pesticide in air between 0.8 and 1.3 m above the top of the potato ridges. Average crop height = 0.5 m

Time	Concentration difference (µg m^{-3})	
(d)	Parathion	Chlorothalonil
0.60	2.14	0.09
0.67	1.72	0.10
0.73	1.17	0.09
0.81	1.25	0.06
1.55	1.18	0.14
1.69	1.36	0.21
1.74	0.99	0.17
2.59	0.39	0.07
2.65	0.42	0.08
3.65	0.13	0.12
3.69	0.08	0.09
7.49	0.008	0.05
7.58	0.018	0.04

Zero time = August 18, 1993, 0.00 h (Central European Summer Time).

Table A3.4 Data on wind speed and air temperature as used for the aerodynamic method

Time	Wind speed (m s^{-1}) at		Δ(Wind speed)	Air temperature 0.8 m	Δ(Air temperature)
(d)	1.3 m	0.8 m	(m s^{-1})	(°C)	(°C)
0.60	1.918	1.573	0.344	20.45	0.185
0.67	1.897	1.563	0.334	21.23	0.202
0.73	1.751	1.409	0.342	19.62	0.083
0.81	0.979	0.787	0.192	17.56	-0.047
1.55	1.592	1.357	0.235	20.22	0.160
1.69	1.662	1.422	0.240	21.16	0.120
1.74	1.584	1.389	0.195	20.59	0.050
2.59	3.609	2.826	0.783	18.00	-0.022
2.65	3.480	2.727	0.753	18.91	0.035
3.65	2.717	2.299	0.418	20.37	0.138
3.69	2.607	2.254	0.353	19.84	0.164
7.49	2.729	2.181	0.548	15.94	0.175
7.58	3.360	2.634	0.726	15.89	0.090

Zero time = August 18, 1993, 0.00 h (Central European Summer Time).

Table A3.5 Data on the Richardson number and the correction coefficients as used for the aerodynamic method (Definitions in Majewski et al., 1991)

Time (d)	Richardson number (-)	Correction factor momentum (-)	Correction factor pesticide (-)
0.60	-0.026	0.890	0.738
0.67	-0.030	0.877	0.722
0.73	-0.012	0.944	0.806
0.81	0.022	1.104	1.104
1.55	-0.048	0.826	0.662
1.69	-0.035	0.862	0.704
1.74	-0.022	0.905	0.756
2.59	0.001	1.003	0.892
2.65	-0.001	0.995	0.877
3.65	-0.013	0.938	0.799
3.69	-0.022	0.905	0.756
7.49	-0.010	0.952	0.818
7.58	-0.003	0.985	0.863

Zero time = August 18, 1993, 0.00 h (Central European Summer Time).

Annex 4 Data on the amounts of parathion collected during the sampling periods of the laboratory experiment

Table A4.1 Radioactivity collected from the polyurethane-foam of the upper and lower channels during each sampling period. Zero time = time of application

Time period (h)	Radioactivity (kBq)	Mass volatilized (mg) (%)	Percentage of dosage[a]
0.00 - 1.15	13.06	0.38	2.10
1.15 - 2.15	11.59	0.34	1.86
2.15 - 3.00	9.37	0.28	1.51
3.00 - 5.25	32.41	0.95	5.21
5.25 - 6.17	11.74	0.35	1.89
6.17 - 7.17	10.69	0.31	1.72
7.17 - 20.43	38.71	1.14	6.23
20.43 - 21.43	12.18	0.36	1.96
21.43 - 24.10	13.42	0.39	2.16
24.10 - 25.10	7.33	0.22	1.18

[a] Radioactivity applied to the plants is 100% (621.73 kBq).

Table A4.2 Radioactivity collected on the polyurethane-foam of the upper and lower channels during each sampling period. Zero time = time of application

Time period (h)	Channel[a]	Radioactivity (kBq)
0.00 - 1.15	up	9.32
0.00 - 1.15	low	3.74
1.15 - 2.15	up	7.92
1.15 - 2.15	low	3.67
2.15 - 3.00	up	6.51
2.15 - 3.00	low	2.86
3.00 - 5.25	up	22.51
3.00 - 5.25	low	9.90
5.25 - 6.17	up	8.44
5.25 - 6.17	low	3.30
6.17 - 7.17	up	7.39
6.17 - 7.17	low	3.30
7.17 - 20.43	up	27.79
7.17 - 20.43	low	10.92
20.43 - 21.43	up	9.32
20.43 - 21.43	low	2.86
21.43 - 24.10	up	9.32
21.43 - 24.10	low	4.10
24.10 - 25.10	up	5.28
24.10 - 25.10	low	2.05

[a] up = upper, low = lower