Volatilization of fenpropimorph and clopyralid after spraying onto a sugar beet crop

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ABSTRACT

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Volatilization rates of pesticides were measured with two micrometeorological methods. For fenpropimorph, the highest rates (1.3-3.0% per hour) were measured in the first hours after application. The rate gradually declined to less than 0.01% per hour on the sixth day. Clopyralid had much lower volatilization rates. They were highest (0.1% per hour) on the day after the day of application and declined below the detection limit (less than 0.01% per hour) on the sixth day after application. Rates calculated with the aerodynamic method were slightly higher than those calculated with the Bowen ratio.

Keywords: crop protection, environmental protection, micrometeorology, pesticide

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Preface

In 1995 DLO Winand Staring Centre and the Institute of Chemistry and Dynamics of the Geosphere 5: Radioagronomy, Forschungszentrum Jülich GmbH (ICG-5, FZJ) carried out a cooperative research project for comparing the volatilization rates of pesticides from a bare soil, measured with methods developed by the two institutes. The somewhat divergent results prompted the continuation of the cooperative research with a similar comparison of the volatilization rates of pesticides after spraying onto a crop. The research project at SC-DLO, in the scope of the Long-term Crop Protection Plan, had to be stopped in the second half of 1995, which made co-operation on a volunteer basis no longer possible. Therefore, ICG-5, FZJ asked SC-DLO to do a field experiment on a contract basis. In this field experiment the volatilization rates of two pesticides (fenpropimorph and clopyralid) from a crop had to be measured on the experimental field near Merzenhausen, with meteorological data transfer facilities to the wind tunnel equipment at the ICG-5, FZJ station. The task of ICG-5, FZJ was to measure the volatilization rates in the wind tunnel parallelly. This report gives the results of the field experiment, mainly carried out by SC-DLO in June 1996. The results of this field study will be compared with that of the windtunnel in a manuscript for an appropriate journal.

The authors would like to thank Mr. H.G. Weitz for the pleasant co-operation and hospitality. We also would like to thank DowElanco B.V., Wilrijk, Belgium for their interest in this study and the delivery free of charge of their product Matrigon to spray the field.

Summary

Pesticide volatilization from soil and plant surfaces after application is a major source of pesticide residues in the atmosphere, including rain, snow and fog. The amount and kinetics of a pesticide volatilizing in time depends on its physio-chemical properties, its formulation, kind and properties of the surface (soil/plant), application technique and environmental factors, such as soil moisture, temperature and wind speed. Deposition of pesticides from the air onto soil and water surfaces may result in adverse effects on terrestrial and aquatic organisms.

Several methods have been developed to measure pesticide volatization, such as laboratory chambers, field methods based on micrometeorological methods and semi-field methods consisting of a wind tunnel placed over a small treated area. It is, however, still uncertain whether the different methods give comparable volatilization rates and if they are representative of the real pesticide volatilization in the field. In 1995, we started a research project to compare the volatilization rate from bare soil measured by micrometeorological methods in the field with the rates measured simultaneously in the wind tunnel at the Institute of Chemistry and Dynamics of the Geosphere 5: Radioagronomy, Forschungszentrum Jülich GmbH (ICG-5, FZJ). This project was continued to determine the volatilization of the fungicide fenpropimorph and the herbicide clopyralid after application onto a sugar beet crop by the Bowen-Ratio (BR) method and the aerodynamic (AD) method.

At 10 times after the field application of fenpropimorf and clopyralid, the concentration gradient of each pesticide above the crop was measured. From measurements on the temperature, humidity and wind speed gradients above the crop, the rate of volatilization of each pesticide was determined with the AD and BR methods. The rate of decline of the fraction of the dosage of each pesticide remaining on the plant leaves was also measured by analysing leaf punches.

The volatilization rate of fenpropimorph was highest during the first hour after its application (3.0 to 2.3% of the dosage per hour) and decreased slightly during the next hours on the day of application. On the first day after the day of application, the volatilization rates decreased to 0.06-0.33% of the dosage per hour. The volatilization rates decreased further to less than 0.01% of the dosage per hour on the sixth day after application. The residues on the sugar beet leaves declined gradually from 68% of the dosage (one hour after application) to 12.8% (6 days after application).

The volatilization rate of clopyralid could not be determined on the day of application and 6 days after application because the concentrations in the air were below or near the detection limits. The volatilization rate was found to be at least lower than 0.02% of the dosage at these two times. On the first, second and third day after the days of application, the hourly volatilization rate was rather constant and amounted to about 0.1% of the dosage. This very unusual course of the volatilization rate in time could not be explained yet. Conversion of the acid clopyralid to more volatile

products (e.g. higher esters), which were than analysed as clopyralid by the derivatization procedure to its methyl ester in the analysis, could be a possibility

There was no correlation with the residue on the leaves. The residues of clopyralid on the sugar beet leaves declined sharply after two rain events with 0.1 mm rainfall each on the second day after the day of application. The residue declined from 66% of the dosage (one hour after application) to 13.7%, probably because part of the highly water-soluble clopyralid was washed off. Thereafter the residue decreased gradually to 2.7% of the dosage at the sixth day after application.

The rinsability of the residues on the leaves was tested by subsequent rinsings of whole leaves with water, methanol and chloroform. One week after application the residue of fenpropimorph was mainly extracted with chloroform, indicating a comparatively high penetration into the leaves. After a week, the very low residue of clopyralid could still be rinsed off with water.

The results of the field experiment will be compared with those of the wind tunnel experiment and the conclusions will be given in a publication drafted by ICG-5, FZJ.

1 Introduction

At the Institute of Chemistry and Dynamics of the Geosphere 5: Radioagronomy, Forschungszentrum Jülich GmbH (ICG-5, FZJ) a wind tunnel was developed to measure gaseous emissions of chemicals and pesticides from agro-ecosystems on a semi-field scale (Stork, 1995, Stork et al., 1994, 1995). However, there is still uncertainty whether (a) the micrometeorological methods give precise information on the actual volatilization rate of a pesticide in the field and (b) the wind tunnel system of the ICG-5, FZJ is representative for reflection of pesticide volatilization in the field.

During 1992-1995 DLO Winand Staring Centre (SC-DLO) has done research on the emission of pesticides into the air, in the scope of the Long-term Crop Protection Plan. In field experiments, two micrometeorological methods were used for measuring the flux densities of pesticides from bare soil surfaces and from crops. In addition, a box method was used to measure the flux density from soil surfaces (Bor et al., 1995, Van den Berg et al., 1995)

In 1995, a cooperative research project of SC-DLO and ICG-5, FZJ was started to compare the volatilization rates of pesticides from a bare soil measured in the field with two micrometeorological methods with that measured under similar conditions in the ICG-5, FZJ system (with on-line transfer of climatic data from the field to the wind tunnel system). Although the climate simulated in the wind tunnel system seemed to differ only slightly from that in the field, measured volatilization rates in the field were roughly 10 times higher at parallel sampling periods (Stork et al., 1996).

These divergent results prompted the continuation of the cooperative research with a similar comparison of the volatilization rates of pesticides after spraying onto a crop. The research project at SC-DLO, in the scope of the Long-term Crop Protection Plan, had to be stopped in the second half of 1995, which made cooperation on a volunteer base not longer possible. Therefore, ICG-5, FZJ asked SC-DLO to do a field experiment on a contract basis. In this field experiment the volatilization rates of two pesticides (fenpropimorph and clopyralid) from a crop had to be measured on the experimental field near Merzenhausen, with meteorological data transfer facilities to the wind tunnel equipment at the ICG-5, FZJ station. The task of ICG-5, FZJ was to measure the volatilization rates in the wind tunnel simultaneously.

The volatilization measurements had to be performed with oil seed rape in the Autumn of 1995. However, extremely dry weather conditions prevented the development of a suitable rape crop on the experimental field near Merzenhausen (with data transfer facilities). After the cold winter of 1995/'96, all leaves were frozen and development of the remaining plants to a crop suitable for the volatilization experiment seemed doubtfull. Recovery of the plants certainly would have taken a comparatively long time. After that time it would have been impossible to sow an alternative crop (e.g. sugar beets). In a discussion on the field in February 1996, with all contracting parties, it was decided to plough the field and to perform the experiments with sugar beets, following a slightly modified research protocol.

The set up and execution of the field experiment of this cooperative project are described in chapter 2. The results are discussed in chapter 3, and a short conclusion about the suitability of the calculated volatilization rates for the purpose of the project is given in chapter 4. The results of the field experiment will be compared with those of the wind tunnel experiment in a publication drafted by ICG-5, FZJ.

2 Materials and methods

2.1 Field site and application

The experiment was carried out on a field in Rhineland near Jülich-Merzenhausen, Germany. This field is situated about 10 km from the lysimeter station of the Institute, where the wind tunnel is located. Instruments for online steering of the wind tunnel are also installed there. The north-western part of this field was grown with sugar beets and an area (182 m x 198 m) was selected for the experiment. The location of the field and the experimental area are shown in Figure 1. The landscape around the field was rather open, with only a few obstacles in the north (Haus Brühl, with trees). These can disturb the dispersion pattern of pesticide vapour in the air above and around the treated field when the wind comes from north to north-east. Generally, the field satisfied the conditions set by the methods used to measure the flux densities.

The growth stage and the height of the crop differed slightly; in the western part the crop showed some drought stress, whereas in the eastern part the crop was developed well with highest plants. This resulted in a somewhat different soil coverage by the leaves, which was estimated (at first sight) to range from 75 to 95%. The average height of the sugar beet crop was measured around the meteorological station, which was placed in the centre of the experimental area, to determine the heights for measuring the different meteorological data and for sampling the air. The height was measured with a polystyrene disc (0.8 m diameter) which was placed on the crop and the 'average' height of the crop under the disc was measured through a hole in the centre. At the start of the experiment (25 June), the average height was 0.41 m (s.d. 4.2, n = 42) and 0.42 m (s.d. 2.7, n = 24) on 28 June. During sunny days the leaves bent downwards because of withering, which resulted in a somewhat lower average crop height.

A Douven field sprayer with a computer system was used for pesticide application. The 22 m wide boom was provided with 44 new nozzles (TeeJet XR11003). This type of nozzle was chosen because of the same droplet spectra and it gives about the same volume of spray liquid per hectare as the nozzle installed at the semi-automatic sprayer for application of the lysimeter inside the wind tunnel with two necesary spraying loops. The rate of water release was checked the day before spraying, and appeared to be 0.923 L min^{-1} with a variance coefficient (VC) of 1.8% (n = 10), at a pressure of 1.9 bar, which was slightly higher than the 0.860 L min^{-1} given by the manufacturer. The difference must be assigned to the accuracy of the manometer of the field sprayer.

Shortly before application, the tank was filled with 800 L tap water (checked with a water meter). Subsequently, 4 L formulated fenpropimorph (Corbel 750 EC, Ciba-Geigy, containing 750 g fenpropimorph per litre) and 4 L formulated clopyralid (Matrigon, DowElanco, containing 100 g clopyralid per litre) were added. The flasks and the filling equipment were rinsed with a total volume of 70 L water, giving a

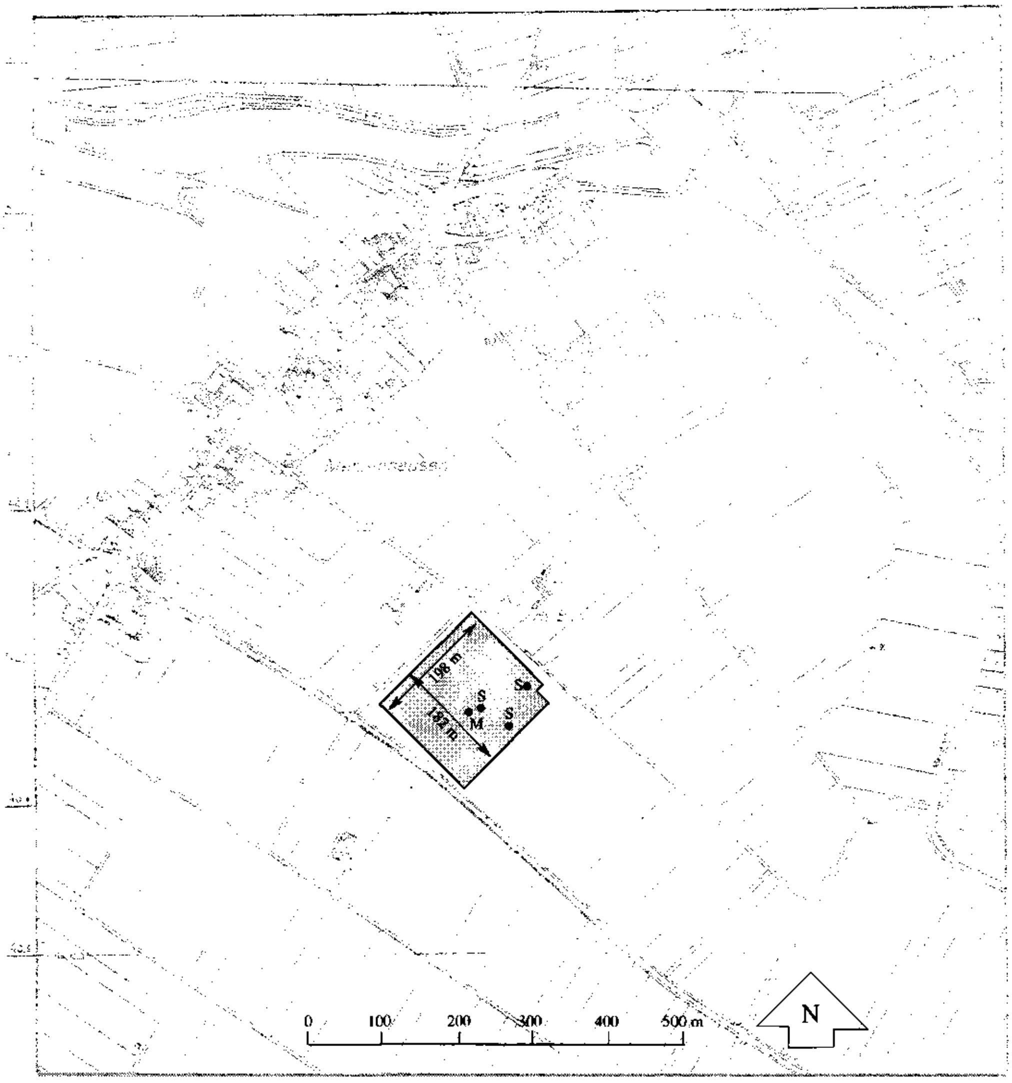


Fig. 1 Location of the field and the treated area (shaded). M = meteorological station. S = air sampling points, depending on main wind direction

total volume of 878 L, which corresponded quite well with the reading on the volume scale indicator on the tank. The dead volume in the pipes and pump system was assumed to be 12 L. This resulted in a total volume of spray liquid of 890 L and calculated concentrations of 3.37 and 0.449 g L^{-1} for fenpropimorph and clopyralid, respectively. Before the start of the experiment, tests were done in the laboratory to check whether the two formulated products could be applied as a mixture. The mixture of both formulated products in water was found to be stable for more than two days; there was no distinct visual process (e.g. sedimentation). Some physico-chemical properties of the active ingredients are given in Table 1.

Table 1 Some physico-chemical properties of clopyralid and fenpropimorph at 20 °C, (after Tomlin, 1994)

Pesticide	Molecular mass (g mol^{-1})	Water solubility (mg L^{-1})	Vapor pressure (mPa)	Henry's law constant (-)
clopyralid	192.0	7850	1.33 [a)]	$1.6 \cdot 10^{-11}$
fenpropimorph	303.5	4.3	2.3	$7.8 \cdot 10^{-5}$

[a)] At 24 °C.

The marked test area (Fig.1) was sprayed on 25 June 1996 between 14.40 to 15.13 h. The wind speed (about 1.5 m s^{-1}) and the wind direction (North-west, parallel with the driving direction in the length of the field) provided a uniform distribution of the spray liquid. During spraying, the driving speed (5.2 km h^{-1}) and spraying pressure (1.9 bar) were fairly constant. The driving speed was checked by the computer as well as by recording the time elapsed over measured distances with a stopwatch. The average driving speed and the measured water release from the nozzle at 1.9 bar, corresponded to an areic spray volume of 212 L ha^{-1}. After spraying the test area, a volume of 150 L remained in the tank (as read from the volume scale on the tank). The volume of liquid sprayed (878 L - 150 L = 728 L) divided by the net sprayed area of 3.54 ha (9 spray tracks of 22 m width and 182 m length, minus a non-sprayed plot of 22 m x 29 m in the eastern part occupied by instruments of ICG-5, FZJ gives a calculated liquid application of 205 L ha^{-1}. With this spray volume and the calculated concentrations in the spray liquid, the rates of application were calculated to be 691 and 92.1 g ha^{-1} for fenpropimorph and clopyralid, respectively.

The concentration of each pesticide in the spraying solution was checked by taking samples from the tank and from the liquid released by the outermost nozzle during spraying. Two samples were taken at the start of the application; a second series of samples was taken at the end of the application. Subsamples of 2.5 ml were taken in the field and added immediately to glass flasks with 50 mL methanol. The flasks were shaken manually for a few min and further shaken on a mechanical shaker for 30 min and stored cool until analysis. The concentration of fenpropimorph in these samples amounted to 114% (s.d. = 2.8) of the calculated concentration for the spraying solution. The concentration of clopyralid in these samples amounted to 107% (s.d. = 7.6) of that calculated for the spraying solution. As the measured concentrations corresponded quite well with those calculated from the mass of pesticide in the formulated product and the estimated total volume in the spraying equipment, correction on the areic masses applied was considered to be unnecessary.

2.2 Methods to measure the rate of volatilization

The aerodynamic and Bowen ratio methods were used to determine the source strength of the emission of fenpropimorph and clopyralid into the air. 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 surface at which an air sample is taken to measure the concentration of pesticide. 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 three heights (0.7, 0.9, and 1.2 m above the soil surface). Two heights were the same as used for measuring the wind speed gradient.

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 multiplying the sensible heat flux density with the vertical air temperature gradient measured. The rate of volatilization of pesticide is calculated from this coefficient and the measured vertical gradient of the pesticide concentration 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 m above the average crop height. As the soil heat flux density is measured at a depth of 0.08 m, a correction needs to be made to account for the heat stored or released in the top 0.08 m soil layer, thus enabling calculating of the soil heat flux density at the soil surface. For this calculation procedure, the average soil bulk density and the average soil moisture content are needed. The soil bulk density was measured around the meteorological station, by taking 100 cm^3 undisturbed soil cores with steel cutting rings. It was found to be 1157 kg m^{-3} (s.d. 53, n = 16). The soil moisture content was 0.087 g g^{-1} dry soil in the period 25 to 29 June and raised to 0.124 g g^{-1} after rainfall on 1 July .

2.3 Meteorological measurements

A tripod with cup anemometers and a wind vane was placed in the centre of the treated area. The (smoothed) soil surface 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, 0.7, 1.2 and 2.0 m above the soil surface. The wind direction was measured with a wind vane (Vector Instruments potentiometer, type W200P) at 2.5 m. The dew point of the air was measured at 0.7 and 1.2 m above the ground with a chilled mirror hygrometer (General Eastern, type Dew-10). The air temperature was measured at the same heights with a system of paired chromel-constantan thermocouples (Campbell Scientific, type 107, diam. 0.1 mm, minimum accuracy 0.01 °C). The soil heat flux was measured at 0.08 m depth with two heat flux plates (Radiation and Energy Balance Systems Inc., type HFT-1). The net radiation was measured at 1.4 m height with a net radiometer (Radiation and Energy Balance Systems Inc., type Q^*6). The soil temperature was measured at depths of 0.02 and 0.06 m with thermocouples. The course with time of all these meteorological variables was registered with a battery-powered Campbell Scientific 21X micrologger. The wind speed and wind direction was meausured with 10 s intervals after which 10 min averages were calculated and stored. For the BR measurements, 20 min averages were calculated.

Rainfall was measured with an electronic tipping-bucket rain gauge (aperture 200 cm^3, 0.25 mm resolution) within the test field. The data were recorded with a Tattle datalogger. The collected water was also periodically transferred into a measuring flask, which enabled the calibration of the layer of rain water corresponding to one pulse recorded with the datalogger. This method made it possible to record also rainfall of less than 0.25 mm.

2.4 Plant sampling and extraction

2.4.1 Rate of decline of the pesticides on the leaves

The rate of decline of the pesticides on the plants was measured by taking leaf samples at several times after application. The treated field was divided into four sections of identical size. In each section three samples were collected at random at each sampling time. Each leaf sample consisted of 40 punches, cut out of the leaves with sharpened brass tubes of 2.8 cm inner diameter. The punches were taken from sections of the sugar beet leaves, with about horizontal position and not covered by other leaves (at the time of sampling). It was assumed that these parts received the average calculated dosage, because of their horizontal position. However, leaf positions changed with time due to withering of the crop by transpiration on sunny days. Samples were taken at 1 and 4 hours after application and at 1, 2, 3 and 6 days after the day of application. The 40 leaf punches were collected in 500 mL glass flasks with screw caps. A volume of 100 mL of methanol was added and the flasks were shaken at a rate of about 110 cycles min^{-1} for one hour. A fraction of the supernatant solution in each flask (about 20 mL) was transferred into a glass flask with screw cap (with aluminium foil inlay) and these samples were stored at about -20 °C until analysis.

The initial areic mass of the pesticide on the leaves was also estimated in a different way. Before spraying, four polystyrene plates (1.0 m x 0.1 m) were placed horizontally at crop height. On each plate 40 punches of untreated leaves were fixed with pins. Within 10 min after application, the sprayed leaves were pooled per plate and extracted as described above. The results can be compared with the calculated dosage and give an impression of the 'recovery' of the sampling procedure for pesticide formulations sprayed in the field.

The recovery of the extraction procedure and analysis of the pesticides of leaf samples was checked in a preliminary experiment with young sugar beet leaves, sampled in the vicinity of Wageningen. Masses of 400 µg clopyralid and 900 µg fenpropimorf (both dissolved in methanol) were added to 40 punches of the leaves. They were extracted with methanol as described before. The recovery of clopyralid was 103% (s.d. 4.2, n = 3) and that for fenpropimorf was 104% (s.d. 8.2, n = 3).

2.4.2 Rinsability of the pesticide residues

The rinsability of the pesticide residues was determined by rinsing leaves using solvents of decreasing polarity (water, methanol and chloroform). On the day of application and at the end of the experiment, 50 leaves were taken at random and rinsed in batches of about 5 leaves. The leaves were held by their stalks and subsequently immersed for 25 s in each of the three solvents (2 L portions, held in stainless steel containers). During each dip, the leaves were slightly moved up and down and drained as good as possible by swinging before they were dipped in the next solvent.

A subsample (100 ml) of the water rinsing was acidified to pH < 1.0 with HCl (37%) and extracted with an equal volume of dichloromethane. Subsamples of all extracts were stored at - 20 °C until analysis.

2.5 Measurement of the pesticides in air

Two sampling systems were used, one for air sampling upwind of the treated field and the other for measuring the concentration gradient in the air downwind the treated area. Both systems consisted of a vacuum pump with a buffer vessel and a pressure regulator valve. A diagram of the sampling unit and its connections is given in Figure 2. The pumps were powered by 220 V generators. Via a manifold, each air sampling head with XAD-4 adsorbent was connected with the central vacuum vessel. A flow meter plus restriction valve (Brooks Instuments type 8-1307-V, max flow rate 5 m^3 h^{-1}) and a gas meter (Schlumberger, type G 4-250, max flow rate 6 m^3 h^{-1}) were mounted in the plastic connecting tubing line (i.d. 12 mm). The air flow for each sampling head with adsorbent was adjusted with the flow regulator valve. The total air volume sampled in a measuring period was read from the gas meter.

The pesticide vapours were trapped on precleaned polystyrene adsorbent XAD-4 (SERDOLIT®, Serva, research grade), held in sampling heads. The particle diameter of the grains ranged from 0.3 to 1.0 mm and the massic surface area of the XAD was 750 m^2 g^{-1}. The sampling heads were constructed from glass tubes (35 mm inner diameter) with screw thread on both sides (type SVL 42, Sovirel). A diagram of the sampling heads is given in Figure 3. Inside a glass tube, a stainless steel wire netting (0.1 mm mesh width) was placed. This tube was provided with 10 g XAD-4 adsorbent, resulting in a layer about 2 cm thick. The tube with adsorbent was placed

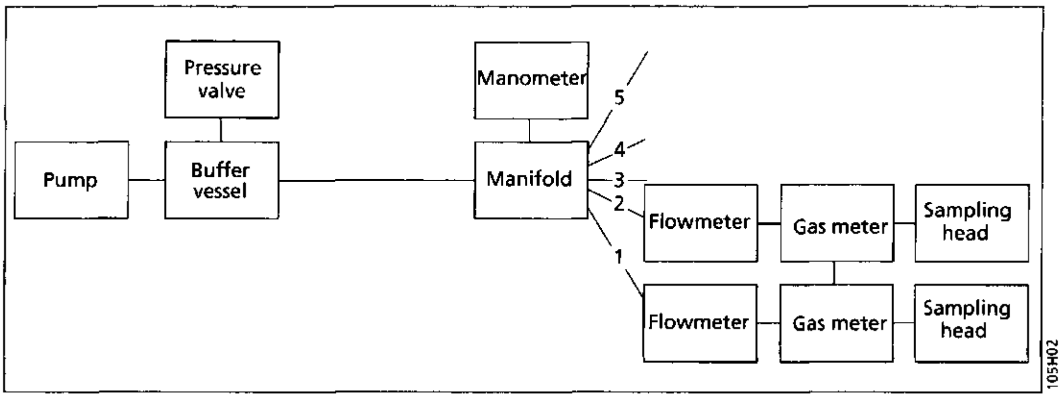


Fig. 2 Diagram of the sampling system.

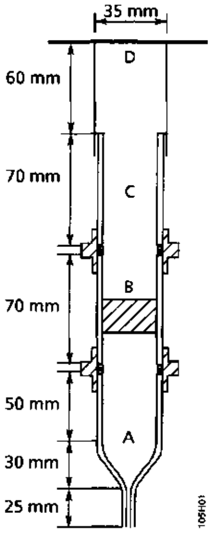


Fig. 3 Construction of the sampling head. A = conical glass tube. B = glass tube with wire netting and XAD-4 adsorbent. C = glas tube. D = aluminium rain shield

vertically on a coupling unit that was connected to one of the gas meters in the sampling system. Another glass tube with the same diameter was screwed on top of the tube with adsorbent to prevent the adsorbent for blowing out by strong wind gusts. The glass tubes were connected to each other with SVL 42 coupling units provided with PTFE-wrapped rubber rings to ensure gas-tight connections between the glass tubes. In case of rainfall, an aluminium plate (10 cm x 10 cm on a tripod) could be placed on the upper glass tube to prevent raindrops falling into the sampling head.

The retention of fenpropimorph and clopyralid by the adsorbent XAD-4 was checked in a preliminary laboratory experiment. A volume of 100 µL solution of methanol containing both pesticides was spread over the surface of 10 g XAD-4 in a sampling head. Three heads were spiked with 1 µg pesticide and another three with 10 µg. A second sampling tube with 5 g XAD-4 was placed in series with each of the heads spiked with 10 µg for checking breakthrough. Subsequently an air flow of 3 $m^3 h^{-1}$ was drawn through the heads for two hours, at an air temperature of 20 °C and 70% air humidity. The XAD in the heads was extracted with the method planned for the field samples. The XAD granules were transferred into glass flasks through a glass funnel. The remaining grains were washed out with about 50 ml methanol, which was also used to rinse the inner wall of the sampling tube and the glass funnel. The flasks were stored overnight at room temperature and the contents were transferred into soxhlet extraction units inclusive all-glass timbers and frits. The flasks were thoroughly washed with methanol to assure that all residues were washed into the soxhlet apparatus. The XAD batches were extracted by at least 10 cycles. The total volume of the extract (about 100 ml) was recorded (by weight) and the extract stored at -20 °C in tight glass flasks until GC analysis. The average recovery of fenpropimorph from the XAD was measured to be 101% of the mass added (s.d. = 10.4), that of clopyralid was measured to be 109% (s.d. = 5.1). There was no clear difference between the recoveries for the 1 µg and 10 µg dosages. No breakthrough (< 1%) was measured for both pesticides.

Downwind sampling heights were 0.7, 0.9 and 1.2 m above the soil surface. The sampling rates were around 3 $m^3 h^{-1}$. The position of the sampling point was adapted to the prevailing wind direction. On the day after the day of application, the wind direction was very variable, chanching from the south throuh the west to the north. Therefore, the sampling point was placed in the centre of the treated area, resulting in an upwind fetch of at least 85 m, but mostly more than 100 m. In the other sampling periods, the sampling point was situated in the south-eastern part of the treated rectangular area, which resulted in an upwind fetch of at least 150 m. The upwind fetches had at least the required distances of 100 times the maximum sampling height of 0.8 m above the crop. Upwind samples were taken at 1.5 m height at a flow rate of about 4 $m^3 h^{-1}$. The position was adapted to the prevailing wind direction and was 15-26 m upwind from the treated area.

On the day of application, four series of one-hour air samples were taken, starting a few minutes after spraying the last track. On the other days, sampling series of two to three hours were taken to attain lower detection limits. Exact sampling times are presented in Table 4.

2.6 Gas chromatographic analysis

2.6.1 Fenpropimorph

Concentrations of fenpropimorph in the methanol extracts of XAD adsorbent and plant leaves were measured with a gas chromatograph (Hewlett Packard, 5890 Series) using a thermoionic nitrogen-phosphorus detector (NPD). Samples of 3 µl were injected in the splitless mode with an HP 7673 autosampler. The gas chromatograph was equipped with a CP-Sil-8, CB column (cross-linked 5% phenyl 95% dimethyl polysiloxane) with a length of 25 m, an i.d. of 0.25 mm and a film thickness of 0.4 µm (Chrompack, Middelburg, The Netherlands). The initial oven temperature was held at 120 °C for 1 min and then increased to 250 °C at a rate of 40 °C min^{-1}. The temperature was maintained at 250 °C for 5 min and then further raised to 280 °C, which was held for 1 min before cooling down to the initial temperature. This temperature program was chosen for quick elution of late peaks. Nitrogen was used as the carrier gas (1 mL min^{-1}). The retention time of the fenpropimorph peak was 8.5 min. Calibration lines for the NP detector were made from solutions of fenpropimorph (analytical grade 96%, PESTANAL®, Riedel de Haën, Germany) in methanol (range 50 to 500 µg L^{-1}). The detection limit was 30 pg.

Subsamples of the soxhlet extracts of XAD-4 were concentrated (5 to 30 times) with the Kuderna Danish method before GC analysis, except the samples taken on the day of application, which had high concentrations of fenpropimorph. Extracts from leaves were diluted 5 to 40 times before injection.

2.6.2 Clopyralid

The trace analysis of clopyralid was performed by derivatization of the pesticide to its methyl ester with borontrifluoride (BF_3) in methanol and gas chromatography using electron-capture detection (GC-ECD). A 2 mL subsample of the concentrated or diluted extracts of XAD and leaves in methanol was transferred into a 10 mL glass tube and the methanol was evaporated to dryness under a stream of nitrogen gas on a water bath at 40 °C. One mL of the reagent (BF_3-methanol, 12% w/w, SIGMA-ALDRICH Chemie B.V. The Netherlands) was added to the tube, which was subsequently covered with a glass ball and placed in a water bath at 60 °C for 30 min. The reaction was stopped by adding 2.5 mL of a saturated NaCl solution in water. The methyl derivative of clopyralid was extracted from the aqueous phase with three subsequent extractions by 2.5 mL n-hexane. The total volume of the collected hexane extract (on average about 7 mL) was recorded (by weight). The hexane extracts were analysed by GC-ECD without further clean-up.

A mass of 2 mg clopyralid (analytical grade 98%, PESTANAL®, Riedel de Haën, Germany) was derivated by the described procedure and taken up in 200 mL hexane. This stock solution was assumed to represent a concentration of 10 mg L^{-1} clopyralid. Standard solutions in hexane (0.5 to 50 µg L^{-1}) were prepared from this stock solution to calibrate the EC detector. The presence of the methyl ester of clopyralid was confirmed with gas chromatography - mass spectrometry (W. Traag, RIKILT-DLO, personal communication, 1995).

The yield of the derivatization method was not constant. To compensate for day-to-day fluctuations in performance, three to four standard solutions of clopyralid in methanol (containing a mass of clopyralid in the range of 4 to 2000 ng) and spiked extracts were also derivated together with each batch of samples. The yield was calculated on the basis of the stock solution of the methyl ester. The methylation efficiency was generally high (80 to 110%), also with XAD extracts spiked with clopyralid. The calculated concentrations of clopyralid equivalent in the extracts were corrected for the yield of the derivatization procedure measured for each batch of samples. Subsamples (40 mL) of the XAD extracts were concentrated with a vacuum rotavapor on a water bath of 40 °C before derivatization. Samples from blank XAD-4 extracts showed no distinct peaks of the methyl ester of clopyralid.

Two mL portions from the methanol extracts of the leaf samples were derivated with the described method and analyzed without clean-up. Portions (2 mL) from extracts of untreated sugar beet leaves from the experimental field were spiked with clopyralid (200 to 2000 ng) and the derivatization yield was measured in a series of sample batches. The average yield was relatively low (72.4%, s.d = 21, n = 15). The calculated concentrations of clopyralid equivalent in the plant extracts were all corrected for this average yield. Samples of untreated leaves did not show peaks of the methyl ester of clopyralid after derivatization of the methanol extracts.

Concentrations of the clopyralid derivative were measured with a gas chromatograph (Carlo Erba HRGC 5360 Series) with an electron-capture detector. Samples of 2 µL were injected in the split mode (split ratio, 1 : 10) with an AS-800 autosampler. The gas chromatograph was equipped with a CP Sil 13, CB column (cross-linked 14% phenyl 86% dimethyl polysiloxane) with a length of 25 m, an inner diameter of 0.25 mm and a film thickness of 0.4 µm (Chrompack, Middelburg, The Netherlands). The oven temperature was 190 °C. Helium was used as the carrier gas (column-head pressure 100 kPa, flow about 1 mL min^{-1}). Nitrogen was used as make-up gas for the EC detector. The retention time of the peak was 4.75 min. Calibration lines for the EC detector were made from (diluted) solutions of the derivative in hexane (range 0.5 to 50 µg L^{-1}). The detection limit for standard solutions was 0.2 pg. However, base-line noise with concentrated extracts of XAD raised the detection limit sometimes to 2 pg (about 3 times the noise level).

3 Results and discussion

3.1 Meteorological data

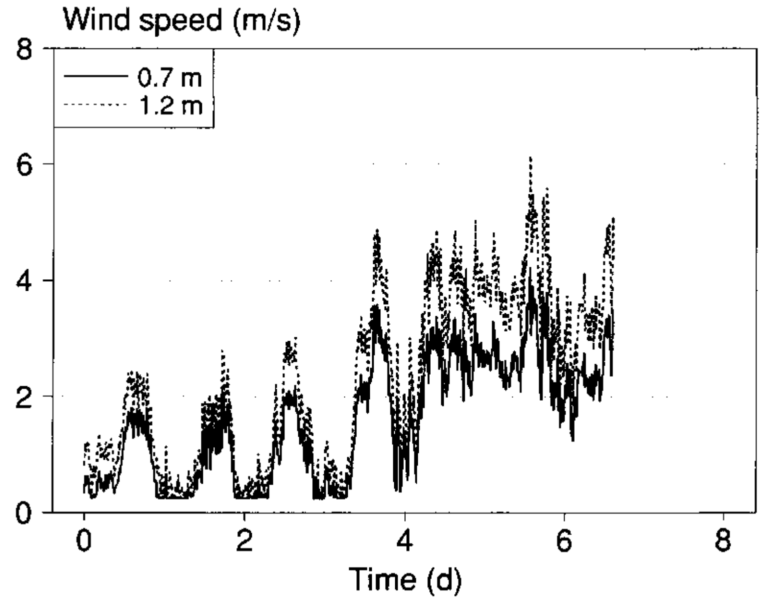
Some characteristic meteorological measurements during the experimental period are presented in Figure 4 and Figure 5. Average values of the essential parameters for calculation of the volatilization rates during air sampling periods with the micrometeorological methods are presented in Annex A. The course with time of the hourly average windspeed at 0.7 and 1.2 m height is given in Figure 4 (top). At the day of application, the wind speed was rather low but fairly constant, with values between 1 and 2 m s^{-1} at 1.2 m height during application and in the following sampling periods until 19.21 h. During three nights after application the wind speed dropped below the lowest measurable value with the cup anemometer (0.2 m s^{-1}). At daytime between the nights, wind speed increased again to values between 1 to 3 m s^{-1}. From the fourth day after the day of application to the last sampling on 1 July, the hourly average wind speed remained fairly constant between 2 to 4 m s^{-1}, also during the nights.

The course of the hourly average air temperature at 0.7 m above ground level (about 0.2 m above the crop) is presented in Figure 4 (bottom). During application and the following air samplings (first day), the air temperature ranged between 15 and 17 °C. After a cold night, the air temperature increased to around 20 °C during the sampling period on the next day. In the sampling periods on the second and sixth day after the day of application, the air temperatures were about the same (16 to 18 °C) as those at the day of application. No temperature data are available for the period between the sampling on the third day after the day of application and the last sampling on 1 July. The very fragile thermocouples were removed because of possible thunderstorms.

The course of the hourly average net radiation is presented in Figure 5 (top). This course roughly corresponds to that for the average air temperature during the first two days. On the first day after the day of application, the net radiation was relatively high with values up to 500 W m^{-2}, which resulted in relatively high air temperatures. The air temperatures at the second and third day after the day of application were rather high, in spite of the lower radiation on these days.

The course of the soil temperature is given in Figure 5 (bottom). The temperature represents the value at 0.04 m depth and it is averaged from the values for the thermocouples at 0.02 and 0.06 m depth. The averaged values are used to calculate the heat stored or released in the top layer, needed for the BR method.

Data on the rainfall during the experimental period are presented in Table 2. Very little rain fell in the night before the day of application and in the morning of the second day after the day of application. A rainy period started after the air samplings on 28 June, resulting in a 12.3 mm cumulative rainfall before the last sampling started on 1 July at 12.00 h.



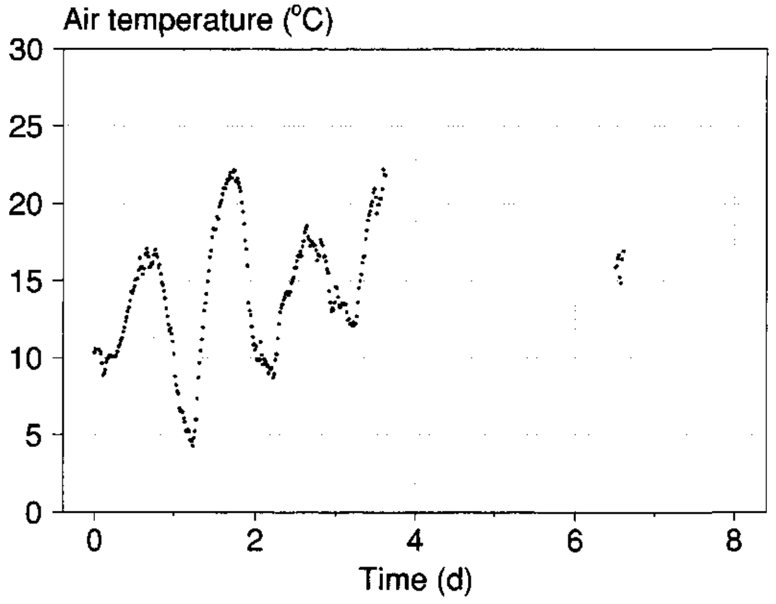


Fig. 4 Hourly average wind speed at 0.7 and 1.2 m above soil surface (top) and average air temperature at 0.7 m (0.2 m above the crop) (bottom) at the experimental field near Merzenhausen. Zero time = 25 June, 1996, 0.00 h

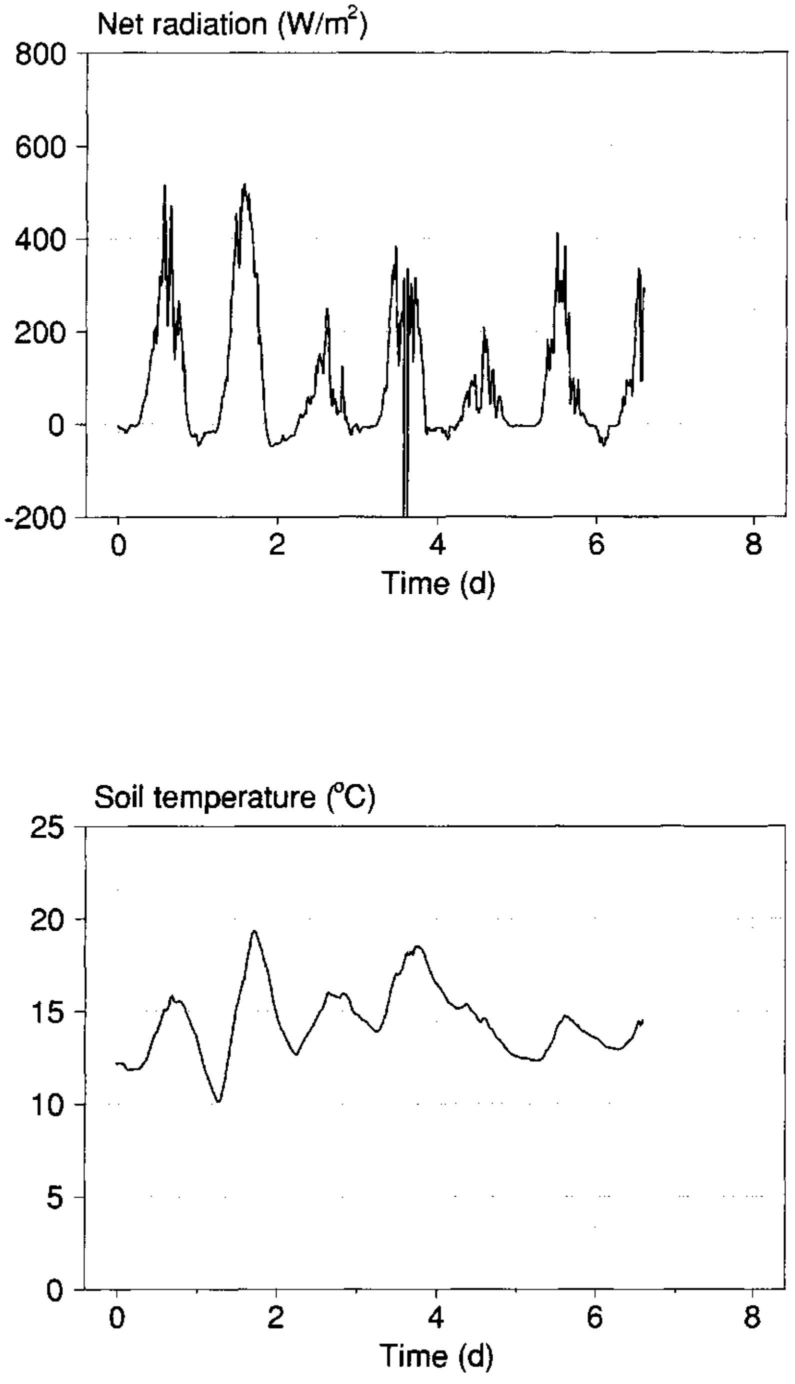


Fig. 5 Net radiation at 1.4 m above soil surface (top) and soil temperature at 0.04 m depth (bottom) at the experimental field near Merzenhausen. Zero time = 25 June, 1996, 0.00 h

Table 2 Rainfall data at the experimental field near Merzenhausen in 1996

Date	Time after application (d) [a]	Period (h)	Rainfall (mm)
23-6		0.00 - 24.00	0.0
24-6		18.00 - 24.00	ca 0.1
25-6	0.0	0.00 - 24.00	0.0
26-6	0.29	0.00 - 24.00	0.0
27-6	1.42	ca 10.00	ca 0.1
	1.80	ca 9.30	ca 0.1
28-6	3.23	22.30 - 24.00	0.75
29-6	3.39	2.30 - 22.30	6.25
30-6	4.48	4.30 - 23.30	1.25
1-7	5.51	5.30 - 6.30	4.00

[a] Start of rain period taken as reference

ca. = about the given values, 0.0 rainfall means 0 or < 0.1

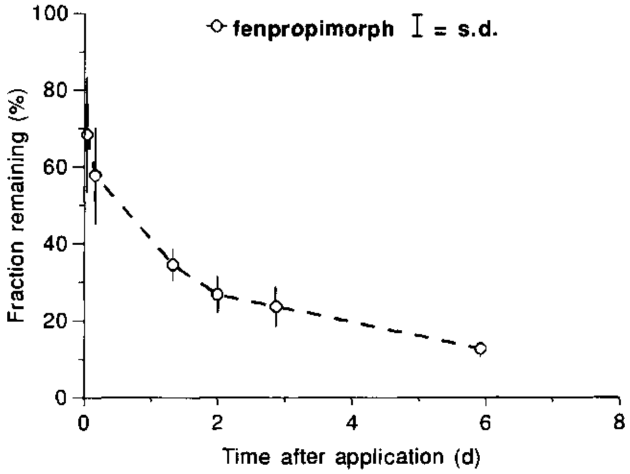
3.2 Plant sampling and extraction

3.2.1 Rate of decline of the pesticides on the leaves

The course with time of the pesticides on the sugar beet leaves (sampled by cutting punches) is given for fenpropimorph in Figure 6 (top) and for clopyralid in Figure 6 (bottom). More detailed information on the fraction of the dosages remaining is given in Annex B. On the first sampling time, about one hour after application, on average 68.4% (s.d. 14.9) and 66.1% (s.d. 9.9) of the calculated dosages were recovered for fenpropimorph and clopyralid, respectively. These comparatively low amounts may be partly caused by the fact that it was not sure that the leaf punches were taken from parts of the leaves, which position were exactly horizontal at the time of application. A deviation from the horizontal position makes that the perpendicular projection has a larger area and consequently a lower areic dosage. The extracted amounts of fenpropimorph gradually decreased with time to an average of 12.8% of the dosage after 6 days. During the first day, the residues of clopyralid decreased somewhat slower than that of fenpropimorph, but the residues of clopyralid decreased sharply after the two rain events with only about 0.1 mm rainfall each on 27 June. Probably part of the highly water soluble clopyralid was washed off. The easy removal of the residue with water rinsings, as described in Section 3.2.2, support this assumption.

The initial areic mass of the pesticides on 40 leaf punches fixed horizontally on polystyrene plates (see Section 2.3.1) was measured to be 82% (s.d. = 15, n = 3) and 97% (s.d. = 15, n = 3) of the calculated areic dosages of fenpropimorph and clopyralid, respectively. One of the four sets of 40 punches on a plate did not show pesticide residues, it was probably situated on a place were the second and third tracks of the spray boom did not join up. The somewhat lower recovery calculated with this method may have several reasons.

- The 40 punches were situated at one spot under the spray boom and vertical or horizontal spray boom movements are well known causes for variability in the dosage.
- The spray solution, catched by the polystyrene plate could ran onder the fixed leaf slices, thus increasing the measured dosage.



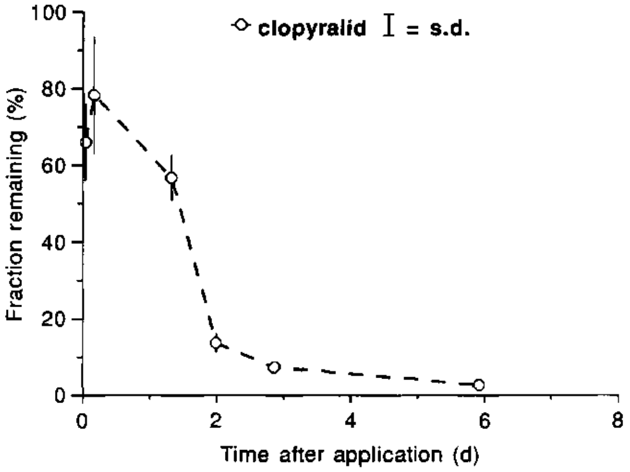


Fig. 6 Decline of the residues of fenpropimorph (top) and clopyralid (bottom) on the sugar beet leaves

- The 'border' effects and the surfaces of the leaf punches, being not flat, resulted in a deviating leaf area than calculated from the diameter of the cutting tube. The high recovery with this method indicates that extraction of the sprayed pesticides from the leaves was effective.

3.2.2 Rinsability of the pesticide residues

The results of rinsing of the whole leaves by three solvents are presented in Table 3. On the day of application, about 4 h after spraying, far the greatest fraction of the residue of fenpropimorph was removed with the methanol rinsing. This indicates that the pesticide had not much penetrated into the wax layer of the leaves. Six days later, the residue was mainly rinsed with chloroform, indicating a high penetration of fenpropimorph into the leaf surfaces.

On the first day, nearly all of the clopyralid residue was rinsed by the water rinsing, which correspons to the high water solubility of this compound. The low amount in the methanol are partly caused by carry over of water to the methanol. After six days a very low amount could be still rinsed with water. However, the increased fractions in the methanol and chloroform rinsings indicated uptake by the leaves.

The ratio between the total masses of the residue of fenpropimorph and clopyralid corresponded well with that found on the 40 leaf punches at the day of application. However, on 1 July the total mass of the clopyralid rinsings was 0.1 to 0.2 times the mass measured in the methanol extracts of the leaf punches. Presumably, methanol could extract part of the clopyralid inside the leaves due to the destruction of the leaves near the rims of the punches and the much longer extraction time.

Table 3 Rinsability of the residues from the leaves by solvents of decreasing polarity

Sampling date	Time after application (d)	Solvent	Mass of pesticide in solvent (mg)	
			fenpropimorph	clopyralid
25 -6	0.16	water	13.27 (25.1 %)[a]	5.00 (91.9 %)
		methanol	32.20 (61.2 %)	0.424 (7.8 %)
		chloroform	7.22 (13.7 %)	0.015 (0.3 %)
1 -7	6.08	water	0.24 (2.5 %)	0.0062 (61.7 %)
		methanol	0.91 (9.6 %)	0.00176 (17.0 %)
		chloroform	8.32 (87.9 %)	0.00215 (21.3 %)

[a] percentage of the total mass rinsed-off by the three solvents

3.3 Concentrations of the pesticides in air

The measured concentrations of the two pesticides in air at the three sampling heights and in the upwind samples are presented in Annex C, Table 1 and Table 2 for fenpropimorph and clopyralid, respectively.

Concentrations of fenpropimorph measured at three sampling heigts are given in Figure 7. The results for the sampling series at the day of application and the day thereafter are given on a different scale (Fig. 7; top) because of the much higher concentration than on the later sampling times (Fig. 7; bottom). There is a linear relationship between the concentration in air and the logarithm of the sampling height, resulting from the naturally logarithmic wind profile.

For each sampling series, the vertical concentration gradient of the pesticide was estimated by calculating the linear regression line through the three data points (correlation coefficient 0.91 - > 0.99). The estimated concentrations at the lowest (0.7 m) and the highest (1.2 m) sampling height were used to calculate the volatilization rate with the micrometeorological methods. This procedure was chosen because the estimated concentration gradients are based on the values of the three measurements and are therefore more accurate.

On the day of application and on the last sampling day, the concentrations of clopyralid in air were below or around the detection limit (2 to 5 ng m^{-3}, depending on the sampled volume of air and the concentration factor). The concentrations of clopyralid measured at the other days are plotted against the logarithm of the sampling height and presented in Figure 8. The data points at each sampling period do not fit so well to straight lines as those for fenpropimorph. This must be ascribed largely to the greater chance for errors in the analysis (with derivatization) of the (very) low concentrations of clopyralid. Thus the small concentration gradient could not be determined directly from the measured clopyralid concentrations with the desired accuracy.

Theoretically, the concentration gradient (slope of the regression line) should be identical for both compounds in a measuring period, since it only depends on the crop, soil and atmospheric conditions. Therefore, the following procedure was adopted to get the best estimation of the concentration gradient of clopyralid. Regression lines were calculated for the three concentrations of clopyralid at each sampling time (correlation coefficient 0.56-0.99). The concentration at a height of 0.9 m was calculated and assumed to represent the 'average concentration level' of clopyralid in the air. The concentrations at 0.7 m and 1.2 m height were then calculated with the slope of the regression line for fenpropimorph in the same period, taking the estimated 'average concentration level' at 0.9 as the reference level. The fit of the measured concentrations of clopyralid with respect to the regression line for fenpropimorph is shown in Figure 8. Differences between the estimated and measured concentrations ranged from +11 to -7% for the sampling series at 26 and 28 June and from +19 to -23% for the two sampling series on 27 June.

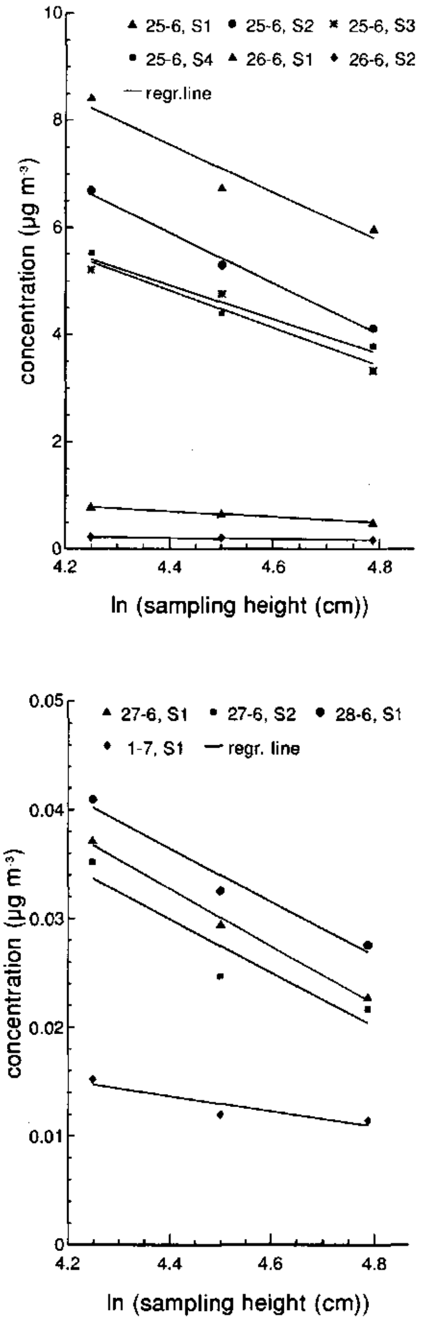


Fig. 7 Concentration profiles of fenpropimorph in air on the indicated sampling dates and series per day (S). The lines are the linear regression lines through the measured concentrations at the three sampling heights

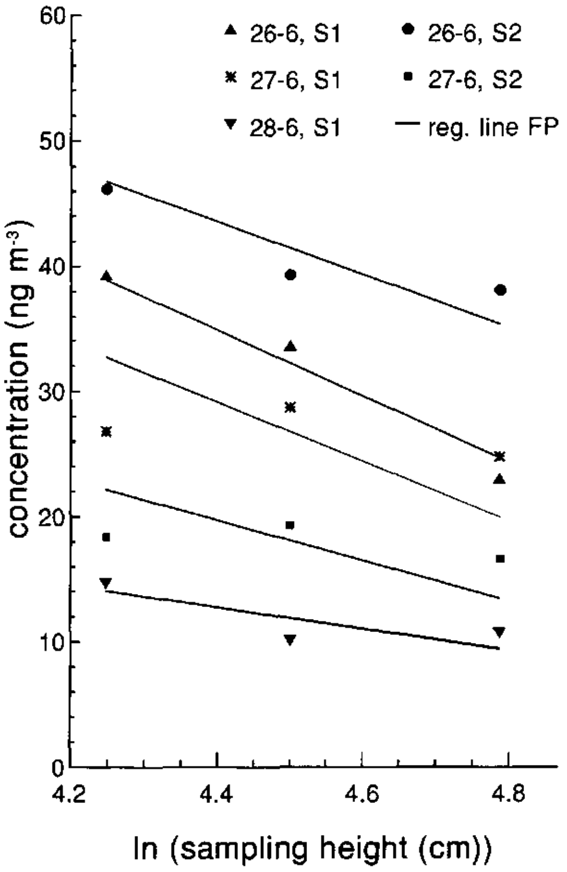


Fig. 8 Measured concentrations of clopyralid in air on the indicated sampling dates and series per day (S). The lines represent the slopes of the regression lines calculated from the concentration profiles of fenproimorph in air in the same period

Concentrations of both pesticides in the upwind air samples were always below the detection limits, except in one case. On the first sampling on the day after application, distinct concentrations of both pesticides were measured in the upwind air (Annex C). At that time the wind direction was very variable and during part of that sampling period the wind was in the direction of the upwind sampling point. For the next sampling on that day the upwind sampling unit was transported to a more suitable place for sampling the air upwind; no pesticides were detected in that sample.

Therefore, no corrections need to be made for concentrations in the upwind air.

The measured concentrations in air were not corrected for recovery because of the nearly 100% recovery in testing the suitability of the XAD for air sampling in the preliminary experiments (see Section 2.5). However, some measurements for fenpropimorph and all measurements for clopyralid were below (2 to 5 times) the lowest level (1 µg) used in the recovery experiment. It is assumed that the lower concentrations were retained by the XAD and extracted from the XAD with a similarly high efficiency as the higher concentrations tested.

3.4 Rate of volatilization

3.4.1 Fenpropimorph

The rates of volatilization of fenpropimorph determined with the AD and BR methods are presented in Table 4. The course with time is also shown in Figure 9 (top). As expected, the volatilization rate was highest shortly after application and it decreased only slightly in time on the day of application. This can be explained by the rather constant meteorological and crop conditions during the four hourly sampling periods on the day of application.

At 1 day after application, the measuring period started at 12.20 h and the leaves had almost completely dried from the dew. The rate of volatilization was found to be considerably lower (1/5 to 1/7 times) than those on the day of application. In the subsequent measuring period at 26 June, the volatilization rate further decreased to about 1/5 times that in the first period. The average air temperature, wind speed and gradient in wind speed were nearly identical during both sampling periods on that day (Annex A). Probably, the decrease in volatilization rate can be explained by the fast decrease of the residue of fenpropimorph on the leaves (e.g. by photodegradation and plant uptake) during the day of application and on 26 June (Fig. 6). The leaf sampling on 26 June was done at the end of the first air sampling period.

At 27 June, 2 days after application, the first measuring period started at 13.00 h. At that time, the lower leaves had not dried yet from the rainfall in the morning. There was a fairly constant wind speed and a rather high wind speed gradient (Annex A). The considerably lower air temperature, as compared to the day before, diminished the volatilization rate. The volatilization rates, as determined with the AD method, decreased from 14.2 µg m^{-2} h^{-1} during the first sampling period to 9.6 µg m^{-2} h^{-1} during the second period.

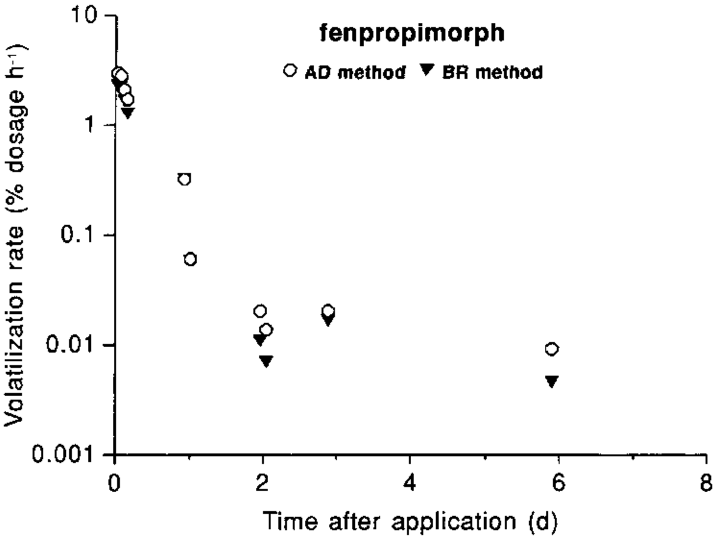
Table 4 Volatilization rates of fenpropimorph determined with the aerodynamic (AD) and Bowen ratio (BR) methods during the first week after application to the sugarbeet crop. Day and time of application: 25 June, 1996, 14.40-5.13 h (Central European Summer Time).

Date	Period	Time after application	Volatilization rate			
			AD method		BR method	
	(h)	(d)	$\mu g\ m^{-2}\ h^{-1}$	%[a]	$\mu g\ m^{-2}\ h^{-1}$	%[a]
June 25	15.13 - 16.15	0.028	2069	2.99	1612	2.33
	16.22 - 17.20	0.076	1961	2.84	1639	2.37
	17.25 - 18.19	0.12	1468	2.12	1183	1.71
	18.25 - 19.21	0.16	1200	1.74	899	1.30
June 26	12.20 - 14.20	0.93	224	0.324	228	0.330
	14.25 - 16.20	1.01	41.9	0.061	40.9	0.059
June 27	13.00 - 15.00	1.96	14.2	0.021	7.24	0.011
	15.04 - 17.00	2.04	9.6	0.014	4.88	0.007
June 28	11.00 - 14.00	2.89	14.2	0.021	11.6	0.017
July 1	12.00 - 14.00	5.92	6.4	0.009	3.21	0.005

[a] percentage of dosage per hour

On 28 June, again the leaves had not dried completely from the little rainfall in the preceeding evening (still water in the depressions of the leaves). The rather high wind speed and gradient in wind speed, and the air temperature of 20 °C enhanced the volatilization rate, which was about the same as the day before. On 1 July, the very low flux densities of fenpropimorph of 6.4 $\mu g\ m^{-2}\ h^{-1}$ (AD method) corresponded well with the low and partly penetrated residues on the leaves at that time (Table 3).

For nearly all sampling periods, the rate of volatilization as calculated with the AD method was higher than that calculated with the BR method. On the day of application and on 26 and 28 June differences were small (AD = 0.9-1.33 times BR); they were greater on 27 June and 1 July (AD = 1.8-2 times BR). Probably, changed weather and crop conditions have different effects on the calculated volatilization rates by the two methods.



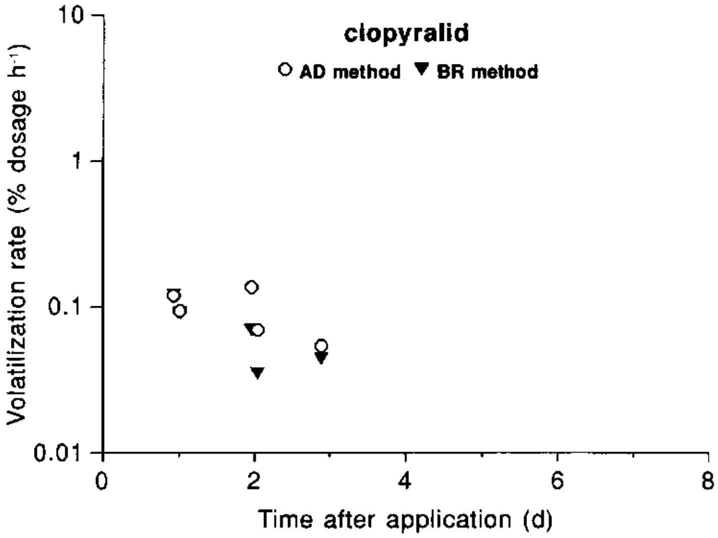


Fig. 9 Hourly flux density of the volatilization of fenpropimorph (top) and clopyralid (bottom) from the sugar beet crop as determined with the aerodynamic (AD) and Bowen-ratio (BR) methods

3.4.2 Clopyralid

The results on the rate of volatilization of clopyralid are given in Table 5 and the course with time is shown in Figure 9 (bottom). At the day of application, clopyralid concentrations in the XAD extracts (from the air samples, about 3 m^3) were below or around the detection limit of the GC analysis. Therefore, no significant concentrations and gradients in concentration of clopyralid could be measured. A maximum value for the volatilization rate was determined with the two micrometeorological methods. The lowest detectable concentration of clopyralid in the air samples was taken as the reference value for calculating the concentration gradient for clopyralid, using the slope of the gradient in the fenpropimoph concentration. These estimated 'detection limit' in concentrations gradient for clopyralid were used as input values for the calculations. However, on the first, second and third day after the day of application, significant concentrations of clopyralid were measured and volatilization rates of 4.98 to 12.58 $\mu g\ m^{-2}\ h^{-1}$ were determined with the AD method. On the last sampling day, concentrations in the air were again below the detection limit, which was about two times lower than on the day of application because of the greater volume of air sampled (about 6.5 m^3). On 26 and 27 June, the volatilization rates of the second sampling series were lower than those of the first series. This corresponds to the decreased rates for fenpropimorph at the second series (Table 4). However, on 26 June the difference was much higher for fenpropimorph.

Table 5 Volatilization rates of clopyralid determined with the aerodynamic (AD) and Bowen ratio (BR) methods during the first week after application to the sugarbeet crop. Day and time of application: 25 June 1996, 14.40-15.13 h (Central European Summer Time)

Date	Period	Time after application	Volatilization rate			
			AD method		BR method	
	(h)	(d)	$\mu g\ m^{-2}\ h^{-1}$	%[a]	$\mu g\ m^{-2}\ h^{-1}$	%[a]
June25	15.13 - 16.15	0.028	<2.73[b]	<0.029	<2.13	<0.023
	16.22 - 17.20	0.076	<2.45	<0.027	<2.05	<0.022
	17.25 - 18.19	0.12	<2.47	<0.027	<1.99	<0.022
	18.25 - 19.21	0.16	<2.23	<0.024	<1.67	<0.018
June 26	12.20 - 14.20	0.93	11.04	0.12	11.25	0.12
	14.25 - 16.20	1.01	8.69	0.094	8.50	0.092
June 27	13.00 - 15.00	1.96	12.58	0.136	6.43	0.070
	15.04 - 17.00	2.04	6.40	0.070	3.24	0.035
June 28	11.00 - 14.00	2.89	4.98	0.054	4.08	0.044
July 1	12.00 - 14.00	5.92	<1.23	<0.013	<0.62	<0.007

[a] Percentage of dosage per hour

[b] (<) means that volatilization rate could not be determined accurately, but was lower than given value. The maximum rate is not constant, it depends on the climatic parameters used by the calculation method and the volume of the air samples

The very unusual course of the volatilization rate of clopyralid during the first days can not be explained easily. There seems to be no correlation with the residue on the leaves, also not after longer time. Volatilization rates were very low shortly after application and identical volatilization rates (Fig. 9, bottom) were calculated for June 26 (about 60% of the dosage remaining) and for June 27 and 28 (about 7% of the dosage remaining). Metabolism of the parent compound on the leaf surface to a more volatile compound, which is than analysed as clopyralid, could result in the observed course of volatilization in time.

4 Conclusions

The concentrations of fenpropimorph in the air samples were relatively high at all sampling times and could be accurately measured. Therefore, the calculated volatilization rates with the AD and the BR method form a good data set to compare with the rates measured in the windtunnel.

The very low concentrations of clopyralid in the air samples and the more complex analysis of this compound resulted in no measurable or less accurate concentration gradients in air and consequently in a few and less accurate volatilization rates. The unexpectedly very low volatilization rate shortly after application and the much higher rates thereafter suggests the conversion of the parent clopyralid into more volatile pruducts, which were analysed as clopyralid. It is thinkable that higher esters of clopyralid are also converted to its methyl ester with the derivatization procedure. This possibility should be proved before the calculated volatilization rates are used to compare with those measured in the windtunnel.

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Annex A Data needed for the calculation of pesticide volatilization rates

Table A.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 after apllication (d)	Soil heat flux at 0.08 m depth (W m^{-2})	Δ (soil temperature) (°C)	Δ (air temperature) at surface (°C)	Bowen ratio coefficient (-)	Soil heat flux (W m^{-2})
0.028	13.29	0.203	0.412	0.357	31.07
0.076	10.17	-0.105	0.068	0.087	0.98
0.12	7.31	0.011	0.166	0.184	8.27
0.16	7.34	-0.038	0.069	0.085	4.05
0.93	22.92	0.214	0.463	0.382	41.69
1.01	24.83	0.336	0.462	0.406	54.26
1.96	8.69	0.141	0.125	0.155	21.00
2.04	10.25	0.019	-0.009	-0.014	11.88
2.89	14.42	0.091	0.084	0.124	22.39
5.92	4.91	0.065	0.012	0.016	10.56

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

Time after application (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})
0.028	381.6	31.07	92.27	258.3	332.3
0.076	184.3	0.98	14.65	168.7	320.0
0.12	232.6	8.27	34.86	189.5	311.3
0.16	158.9	4.05	12.16	142.7	260.6
0.93	485.5	41.69	122.66	321.1	393.4
1.01	455.9	54.26	115.88	285.8	372.6
1.96	179.7	21.00	21.35	137.4	253.3
2.04	91.1	11.88	- 1.15	80.4	182.5
2.89	247.7	22.39	24.80	200.5	437.9
5.92	233.9	10.56	3.51	219.8	433.8

Table A.3 Data on wind speed and air temperature as used for the arodynamic method

Time after application	Wind speed (m s^{-1})		Δ Windspeed	Air temp. at 0.7 m	Δ Air temp.
(d)	0.7 m	1.2 m	(m s^{-1})	(°C)	(°C)
0.028	1.560	2.093	0.533	16.85	0.412
0.076	1.641	2.249	0.608	15.99	0.068
0.12	1.497	2.070	0.573	16.61	0.166
0.16	1.499	2.045	0.547	16.36	0.069
0.93	1.141	1.525	0.385	19.80	0.463
1.01	1.234	1.604	0.370	21.35	0.462
1.96	1.942	2.726	0.784	17.48	0.125
2.04	1.522	2.125	0.604	17.72	- 0.009
2.89	2.136	2.999	0.862	20.33	0.084
5.92	3.064	4.484	1.420	15.94	0.012

Table A.4 Data on the Richardson number and the correction coefficients as used for the aerodynamic method (Definitions in Majewski et al., 1991)

Time after application (d) (-)	Richardson number (-)	Correction factor momentum (-)	Correction factor pesticide
0.028	- 0.025	0.895	0.745
0.076	- 0.003	0.984	0.862
0.12	- 0.009	0.958	0.826
0.16	- 0.004	0.980	0.856
0.93	- 0.052	0.816	0.651
1.01	- 0.056	0.807	0.641
1.96	- 0.003	0.982	0.860
2.04	0.000	1.002	0.890
2.89	- 0.002	0.990	0.871
5.92	0.000	0.999	0.884

Table A.5 Difference in concentration of the pesticides in air between 0.7 and 1.2 m above the soil surface. Values estimated from the measured concentrations at three sampling heights

Time after application (d)	Concentration difference ($\mu g\ m^{-3}$)	
	fenpropimorph	clopyralid
0.028	2.425	< 0.0032
0.076	2.561	< 0.0032
0.12	1.900	< 0.0032
0.16	1.725	< 0.0032
1.93	0.290	0.0143
1.01	0.0550	0.0114
1.96	0.0143	0.0127
2.04	0.0134	0.00887
2.89	0.0133	0.00466
5.92	0.0037	< 0.00072

Annex B Remaining fractions of the pesticides on the leaves

Table B.1 Residues of fenpropimorph on the sugar beet leaves. Residues in % of dosage of 691 g ha^{-1} (6.91 μg cm^{-2} leaf area)

Date	Time after application (d)	Replicate no	Quadrant				Average of 12 samples
			1	2	3	4	
25 - 6	0.02	1	69.9	85.4	64.6	58.5	
		2	36.9	87.9	74.7	56.7	
		3	52.4	80.8	85.6	67.6	
		average	53.0	84.7	75.0	60.9	68.4
		s.d.	13.5	2.9	8.6	4.8	14.9
25 - 6	0.13	1	39.1	66.8	69.1	67.6	
		2	33.3	67.3	53.1	59.5	
		3	40.7	66.1	65.1	66.3	
		average	37.7	66.8	62.4	64.5	57.8
		s.d.	3.2	0.5	6.8	3.6	12.4
26 - 6	0.93	1	41.6	34.3	38.0	26.9	
		2	32.1	32.3	29.7	31.5	
		3	39.1	37.1	35.8	36.5	
		average	37.6	34.6	34.5	31.6	34.6
		s.d.	4.0	2.0	3.5	3.9	4.0
27 - 6	1.95	1	26.3	30.8	31.8	29.4	
		2	25.8	26.9	30.5	-	
		3	18.6	16.9	26.3	31.1	
		average	23.6	24.9	29.5	30.2	26.8
		s.d.	3.5	5.8	2.3	0.9	4.7
28 - 6	2.84	1	23.4	30.6	22.1	22.0	
		2	22.4	26.4	27.8	23.4	
		3	11.8	32.3	18.9	23.3	
		average	19.2	29.8	23.0	22.9	23.7
		s.d.	5.2	2.5	3.7	0.6	5.1
1 - 7	5.88	1	11.6	14.6	12.6	11.2	
		2	12.6	13.7	15.4	17.4	
		3	11.0	12.8	10.4	9.8	
		average	11.7	13.7	12.8	12.8	12.8
		s.d.	0.7	0.7	2.0	3.3	2.1
26 - 6		untreated 1					< 0.63
		untreated 2					< 0.63
		untreated 3					< 0.63

Table B.2 Residues of clopyralid on the sugar beet leaves. Residues in % of the dosage of 92.1 g ha^{-1} (0.921 µg cm^{-2} leaf area)

Date	Time after application (d)	Replicate no	Quadrant				Average of 12 samples
			1	2	3	4	
25 - 6	0.02	1	73.1	77.4	67.2	63.2	
		2	43.8	65.9	58.6	57.5	
		3	67.2	78.9	61.6	79.0	
		average	61.3	74.1	62.5	66.6	66.1
		s.d.	12.7	5.8	3.6	9.1	9.9
25 - 6	0.13	1	58.0	92.1	73.0	82.8	
		2	57.7	92.6	55.0	84.8	
		3	63.7	94.4	93.9	92.7	
		average	59.8	93.1	74.0	86.7	78.4
		s.d.	2.8	1.0	15.9	4.3	15.2
26 - 6	0.93	1	58.3	56.5	61.0	43.3	
		2	57.8	56.9	64.1	56.1	
		3	65.5	57.3	57.1	48.0	
		average	60.5	56.9	60.7	49.1	56.8
		s.d.	3.5	0.4	2.9	5.3	5.9
27 - 6	1.95	1	15.6	12.9	15.1	15.4	
		2	15.0	15.3	13.3	-	
		3	8.7	9.6	13.9	15.9	
		average	13.1	12.6	14.1	15.6	13.7
		s.d.	3.1	2.3	0.7	0.2	2.3
28 - 6	2.84	1	5.8	8.4	10.1	6.6	
		2	7.1	6.4	8.1	8.0	
		3	4.5	9.0	7.4	7.8	
		average	5.8	7.9	8.6	7.5	7.4
		s.d.	1.1	1.1	1.2	0.6	1.4
1 - 7	5.88	1	1.6	3.4	3.2	2.4	
		2	2.5	3.9	2.4	3.1	
		3	2.2	2.4	2.1	2.7	
		average	2.1	3.3	2.5	2.8	2.7
		s.d.	0.4	0.6	0.5	0.3	0.6
26 - 6		untreated 1					< 1.16
		untreated 2					< 1.16
		untreated 3					< 1.16

Annex C Concentrations of fenpropimorph and clopyralid measured in air

Table C.1 Concentrations of fenpropimorph measured in air at the three sampling heights and upwind. Day and time of application: June 25, 1996, 14.40 - 15.13 h .

Date	Sampling period (h)	Time after application (d)	Concentration ($\mu g\ m^{-3}$)			
			0.7 m	0.9 m	1.2 m	Upwind
June 25	15.13 - 16.15	0.028	8.43	6.74	5.98	
	16.22 - 17.20	0.076	6.69	5.30	4.12	< 0.004 a)
	17.25 - 18.19	0.12	5.21	4.76	3.33	
	18.25 - 19.21	0.16	5.53	4.39	3.79	< 0.004 a)
June 26	12.20 - 14.20	0.93	0.790	0.658	0.500	0.068
	14.25 - 16.20	1.01	0.220	0.208	0.166	< 0.004
June 27	13.00 - 15.00	1.96	0.0372	0.0295	0.0228	< 0.004
	15.04 - 17.00	2.04	0.0355	0.0247	0.0217	< 0.004
June 28	11.00 - 14.00	2.89	0.0410	0.0326	0.0276	< 0.004
July 1	12.00 - 14.00	5.92	0.0152	0.0120	0.0114	-

a) 2 h measuring period upwind

\- no upwind measurement

Table C.2 Concentrations of clopyralid measured in air at the three sampling heights and upwind. Day and time of application: June 25 1996, 14.40 - 15.13 h .

Date	Sampling period (h)	Time after application (d)	Concentration ($\mu g\ m^{-3}$)			
			0.7 m	0.9 m	1.2 m	Upwind
June 25	15.13 - 16.15	0.028	< 0.005	± 0.008	± 0.012	
	16.22 - 17.20	0.076	< 0.008	± 0.008	< 0.009	< 0.0025 a)
	17.25 - 18.19	0.12	< 0.005	± 0.013	< 0.005	
	18.25 - 19.21	0.16	< 0.006	+ 0.012	< 0.009	< 0.0025 a)
June 26	12.20 - 14.20	0.93	0.0393	0.0336	0.0230	0.0084
	14.25 - 16.20	1.01	0.0462	0.0393	0.0381	< 0.0025
June 27	13.00 - 15.00	1.96	0.0268	0.0287	0.0247	< 0.0025
	15.04 - 17.00	2.04	0.0184	0.0193	0.0166	< 0.0025
June 28	11.00 - 14.00	2.89	0.0147	0.0101	0.0107	< 0.0020
July 1	12.00 - 14.00	5.92	<0.0025	< 0.0025	<0.0025	-

a) 2 h measuring period upwind

\- no upwind measurement