

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

### Determination of volatilization (dissipation) and secondary deposition of pesticides in a field study using passive dosimeters

Anette Ravn Jensen<sup>a</sup>; Niels Henrik Spliid<sup>a</sup>; Bo Svensmark<sup>b</sup>

<sup>a</sup> Institute of Integrated Pest Management, University of Aarhus, DK-4200 Slagelse, Denmark <sup>b</sup> Copenhagen University, Universitetsparken 4, 2100 Copenhagen Ø, Denmark

Online publication date: 18 November 2010

**To cite this Article** Jensen, Anette Ravn , Spliid, Niels Henrik and Svensmark, Bo(2007) 'Determination of volatilization (dissipation) and secondary deposition of pesticides in a field study using passive dosimeters', *International Journal of Environmental Analytical Chemistry*, 87: 13, 913 – 926

**To link to this Article:** DOI: 10.1080/03067310701455955

**URL:** <http://dx.doi.org/10.1080/03067310701455955>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Determination of volatilization (dissipation) and secondary deposition of pesticides in a field study using passive dosimeters

ANETTE RAVN JENSEN<sup>†</sup>, NIELS HENRIK SPLIID<sup>\*†</sup>  
and BO SVENSMARK<sup>‡</sup>

<sup>†</sup>Institute of Integrated Pest Management, University of Aarhus,  
Forsøgsvej 1, DK-4200 Slagelse, Denmark

<sup>‡</sup>Copenhagen University, Universitetsparken 4, 2100 Copenhagen Ø, Denmark

*(Received 18 December 2006; in final form 15 May 2007)*

The volatilization and secondary deposition of the herbicides prosulfocarb and pendimethalin were measured using passive dosimeters with Chinese cabbage and soil as collective material. Passive dosimeters were placed in the field before spraying and at three distances downwind after spraying. The volatilization of prosulfocarb and pendimethalin determined as dissipation was 80 and 60% of the applied amount from the cabbage surface, while no significant loss was measured from soil surfaces after 48 h. The secondary deposition of prosulfocarb and pendimethalin 25 m from the spray zone was 2 and 4% on the leaf surface as well as on the soil surface. At 5 m distance, 6 and 10% of the field dose of prosulfocarb and pendimethalin could be determined on dosimeters with leaves, and 4 and 8% of the field dose could be determined on soil surfaces.

*Keywords:* Prosulfocarb; Pendimethalin; Volatilization; Secondary deposition; Leaves; Soil

### 1. Introduction

The presence of pesticides in rainwater all over Europe has been reported through the 1990s [1]. The presence of atrazine, isoproturon, terbutylazine, MCPA and mechlorprop [2] and pendimethalin, bromoxynil, and ioxynil [3] in rainwater over Denmark was reported. Prosulfocarb, pendimethalin, and diflufenican were reported in rainwater in Swedish research [4].

The presence of pesticides in rainwater confirms that pesticides disappear from the sprayed fields to the atmosphere due to volatilization, drift, or soil erosion [5]. Plimmer [6] claims that only 1–3% of the applied amount of pesticides reaches the crops in the sprayed field. The volatilization rate of a pesticide depends among other things on the physical–chemical properties of the active ingredient and the environmental conditions of the crop or soil surface [7].

\*Corresponding author. Fax: +45-89993501. Email: niels.spliid@agrsci.dk

The volatilization rate of the active ingredient is often higher from crop surfaces than from soil surfaces [8]. The volatilization of lindane was 38–58% from bean leaves *versus* 28% from bare soil [9]. The volatilization of endosulfan was 12% from soil surfaces *versus* 60% from bean leaves [10]. The knowledge of volatilization from plant surfaces is limited compared with the knowledge of volatilization from soil [11].

Different methods have been developed to measure volatilization of pesticides. Micro-meteorological methods can be used to estimate volatilization fluxes from both soil and crop surfaces in a sprayed field. During the experiment, a sampling mast measures the air concentration, wind speed and direction, air temperature, and several other parameters. Volatilization fluxes from both soil and plant surfaces can be estimated from the measured environmental conditions [12]. Semi-field systems have been developed as a cheaper supplement to the micro-meteorological methods. The system consists of a lysimeter with either the soil or plant surface, which is sprayed and placed in a wind tunnel with a constant wind speed. Air sampling is performed, and the amount of volatilized pesticide can be measured in the air stream [11]. Volatilization of pesticides can also be measured in laboratory systems; these are of different constructions, e.g. a volatilization chamber, which can be set up to measure volatilization from both soil and plant surfaces [7]. Finally, the volatilization of pesticides can be measured using passive dosimeters with various types of collective material [13].

A pesticide can be deposited outside the sprayed area as either primary or secondary deposition [14]. Primary deposition is due to drift during and right after spraying; and secondary deposition is due to volatilization from soil and leaf surface after spraying [14]. Primary deposition of pesticides has for instance been measured with the use of passive dosimeters with glass as collective material [13] and with paper as collective material [15].

The aim of the present study was to gain knowledge about the volatilization and secondary deposition of the two pesticides prosulfocarb and pendimethalin, which both have relatively high vapour pressures. The volatilization and secondary deposition were determined using passive dosimeters in a field experiment where the herbicides were sprayed under normal agricultural practices. Passive dosimeters with collective surfaces of either soil or leaf were placed in the application zone before spraying, and passive dosimeters were placed downwind of the application zone after the application to avoid any contributions of primary deposition due to drift. The soil and leaf samples were analysed with liquid chromatography and mass spectrometric detection.

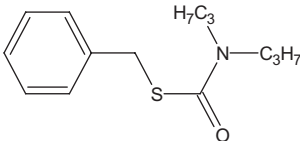
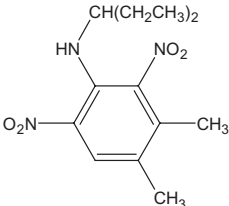
## 2. Experimental

The field experiment was performed at the Flakkebjerg Research Centre (55° 19' N, 11° 23' E), Zealand, Denmark. The spraying was performed as a part of the normal agricultural practice for weed control in the autumn by the agricultural staff at the Research Centre.

The field was sprayed with prosulfocarb and pendimethalin. The physical and chemical data for the compounds are displayed in table 1.

The volatilization and secondary deposition of the two active ingredients were measured with passive dosimeters with soil or Chinese cabbage leaves as collective material. The soil and the cabbage surfaces were chosen to simulate the volatilization

Table 1. Physical and chemical data for the active ingredients.

| Active ingredient                                                                 | Prosulfocarb                                                                      | Pendimethalin                                                                      |
|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|
| Product                                                                           | Boxer                                                                             | Stomp                                                                              |
| Manufactory                                                                       | Syngenta Crop Protection                                                          | BASF                                                                               |
| Chemical structure                                                                |  |  |
| IUPAC name                                                                        | <i>S</i> -Benzyl dipropylthio carbamate                                           | <i>N</i> -(1-Ethylpropyl)-2,6-dinitro-3,4-xylidine                                 |
| Molecular formula                                                                 | C <sub>14</sub> H <sub>21</sub> NOS                                               | C <sub>13</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub>                      |
| CAS number                                                                        | 52888-80-9                                                                        | 40487-42-1                                                                         |
| Molecular weight (g mol <sup>-1</sup> )                                           | 251.4                                                                             | 281.3                                                                              |
| Form                                                                              | Colourless liquid                                                                 | Orange-yellow crystals                                                             |
| Melting point (°C)                                                                | <-10                                                                              | 54-58                                                                              |
| Solubility in water (mg L <sup>-1</sup> )                                         | 13.2 (20°C)                                                                       | 0.3 (20°C)                                                                         |
| <i>V</i> <sub>P</sub> (mPa)                                                       | 6.9 (25°C)                                                                        | 1.94 (25°C)                                                                        |
| <i>K</i> <sub>H</sub> (Pa m <sup>-3</sup> mol <sup>-1</sup> ) (25°C) <sup>a</sup> | 0.1                                                                               | 0.15                                                                               |
| <i>K</i> <sub>OW</sub>                                                            | 10 <sup>4.7</sup>                                                                 | 10 <sup>5.2</sup>                                                                  |
| <i>K</i> <sub>OC</sub> <sup>a</sup>                                               | 5621                                                                              | 2622                                                                               |

<sup>a</sup>All data are from Tomlin [22] except US EPA EPI-suite ver. 3.11.

and deposition behaviour of pesticides from soil and plant surfaces in a sprayed field and in the border zone. The soil was chosen as a typical Danish agricultural soil. The Chinese cabbage was chosen due to its large area, which could fit onto the bottom-up side of a Petri dish, and the surface is assumed to be similar to the surfaces of many other plants. The soil dosimeter consisted of a Petri dish, 90 mm in diameter and 14 mm in height, and a 30-cm stick. The same materials were used for the leaf dosimeter, but the Petri dish was fastened to the stick with the bottom up to avoiding the edge of the dish. The cabbage was cut into the dimension of a Petri dish and fastened to the Petri dish with two rubber bands, as shown in figure 1. The soil was a sandy clay loam from the top layer sampled in March 2001 from Askov Research Station, Jutland, Denmark. The soil was air-dried and sieved with a 2-mm sieve and stored at 4°C. The water content was 16%; and the content of organic carbon in the soil was 3.19 g per 100 g of soil. A dosimeter with soil is shown in figure 2.

In total, 132 passive dosimeters were used for the study, of which 66 were equipped with cabbage leaves. Each leaf was fastened with two rubber bands. The exposed soil or leaf samples were collected in 200-mL conical Falcon tubes with a cap (Becton Dickinson Lab Ware, Franklin Lakes, NJ), and 50 mL of methanol, HPLC grade (Rathburn Chemicals, Walkersburn, UK), was added with a dispenser (Fortuna Optifix<sup>®</sup> Basic 25, Wertheim/Main, Germany).

## 2.1 Method

Thirty-six passive dosimeters were placed inside the spray zone before spraying in two lines with 18 dosimeters in each line with approximately 1 m between each line and each dosimeter. The position of the dosimeters can be seen in figure 3. The wind



Figure 1. Dosimeter with Chinese cabbage. Petri dish: diameter 90 mm and height 14 mm.



Figure 2. Dosimeter with soil. Petri dish: diameter 90 mm and height 14 mm.

direction in the figure is from the east. In figure 4, the variation in wind direction during the study is displayed. One leaf was placed on every second dosimeter, and 15 g of soil was placed in the dosimeters in between. The spraying was performed shortly after setting up the dosimeters. A sample of the pesticide mixture in the spray tank was sampled from the bottom of the sprayer tank into a glass bottle and kept at 4°C until analysis. The theoretical content of the active ingredient in the pesticide mixture in the spray tank can be seen in table 2.

Passive dosimeters (18) were placed downwind of the spraying zone 30 min after spraying to avoid contribution from primary drift. The dosimeters were placed 5, 10, and 25 m from the spray zone (figure 3). Three dosimeters with soil and three with cabbage were placed at each distance.

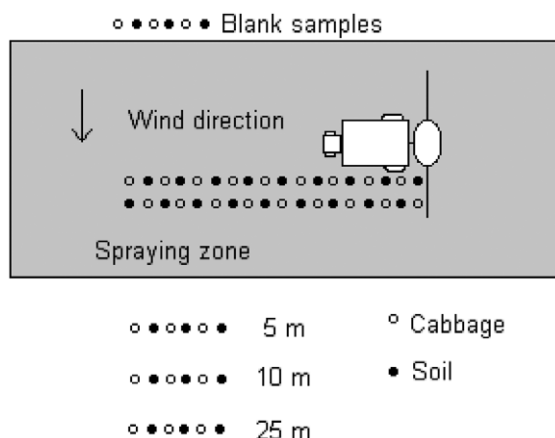


Figure 3. Position of dosimeters in the field experiment.

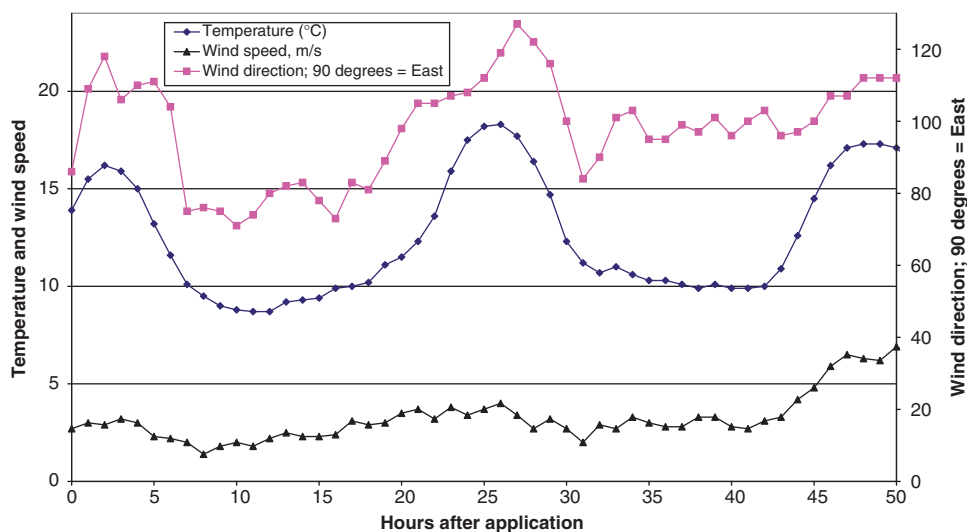


Figure 4. Data on temperature, wind speed, and wind direction. There was no precipitation during the study period. Spraying at 12.50 p.m.

Table 2. Pesticide application: nominal application, analysis of the spray solution, and exposure of the dosimeters: mean  $\pm$  SD ( $\text{g ha}^{-1}$ ) and percentage of spray which reached the target.

| Amount                                 | Prosulfocarb                     | Pendimethalin                   |
|----------------------------------------|----------------------------------|---------------------------------|
| Theoretical content of tank            | 1040 $\text{g ha}^{-1}$          | 132 $\text{g ha}^{-1}$          |
| Analysis of tank content               | 1180 $\pm$ 89 $\text{g ha}^{-1}$ | 150 $\pm$ 12 $\text{g ha}^{-1}$ |
| Exposure of the dosimeter leaf surface | 440 $\pm$ 83 $\text{g ha}^{-1}$  | 36 $\pm$ 7 $\text{g ha}^{-1}$   |
| Exposure of the dosimeter leaf surface | 37 $\pm$ 7% of spray             | 24 $\pm$ 5% of spray            |
| Exposure of the dosimeter soil surface | 783 $\pm$ 88 $\text{g ha}^{-1}$  | 57 $\pm$ 6 $\text{g ha}^{-1}$   |
| Exposure of the dosimeter soil surface | 66 $\pm$ 7% of spray             | 38 $\pm$ 4% of spray            |

Table 3. Information about the spraying.

| The field:                | Spraying equipment                       | Data for application            |
|---------------------------|------------------------------------------|---------------------------------|
| Crop: winter barley       | Nozzle: Hardi 110-02                     | Date: 5–7 October 2005          |
| Height of crop: 10 cm     | Application rate: 150 L ha <sup>-1</sup> | Time for spraying: 12.50 p.m.   |
| Growth stage, BBCH: 11–12 | Height of boom: 50 cm                    | Wind speed: 2 m s <sup>-1</sup> |
| Crop cover: 5–10%         | Length of boom: 12 m                     | Temperature: 13°C               |

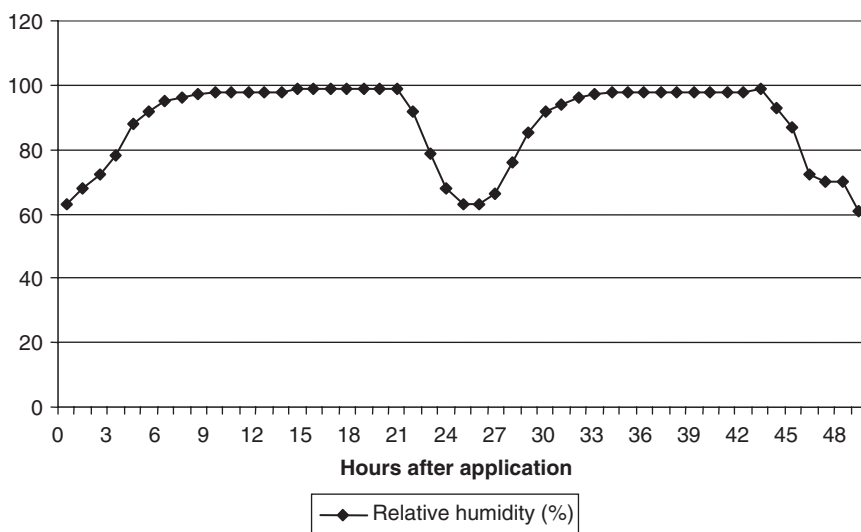


Figure 5. Data on relative humidity.

Three dosimeters with cabbage leaves and three with soil were placed 10 m upwind of the spray zone from hour 24 to 27 for background determination. Inside the spraying zone, sampling was performed right after spraying and 3, 6, 24, 27, and 48 h after spraying. Outside the spraying zone, the dosimeters and collective material were replaced 3.5, 6.5, 24.5, and 27.5 h after spraying, and the last dosimeters were sampled 48.5 h after spraying.

The samples were transferred to Falcon tubes, and 50 mL of methanol was added for extraction. The samples were stored at  $-18^{\circ}\text{C}$  until analysis.

Data on the field and time of spraying and meteorological data during the spraying can be seen in table 3 and figures 4 and 5.

## 2.2 Analysis

The samples from inside the spray zone were diluted 20 times with 50% methanol. The tank sample was diluted 10,000 times with 50% methanol. The samples from outside the spray zone were preconcentrated 10 times on a VR-maxi vacuum centrifuge from Heto. Recovery samples with a theoretical final concentration of  $200\ \mu\text{g L}^{-1}$  were concentrated on the vacuum centrifuge to determine the loss during the concentration process.

After either dilution or preconcentration, the samples were filtered directly into vials with the use of a 2-mL Syringe (BD Plastipak, Becton Dickinson, Madrid, Spain) and single-use, syringe filter, 0.45  $\mu\text{m}$  non-sterile Minisart SRP 15 (Vivascience, Hannover, Germany).

The cabbage and soil samples, blank samples, samples of the tank mixture, matrix spikes in the concentrations 10, 50, and 500 ppb, recovery samples, and blank samples of the matrices were analysed with liquid chromatography and mass spectrometric detection (LC–MS). The LC–MS instrument was a Hewlett Packard 1100 MSD (Palo Alto, CA), and the analytical method was developed in-house at University of Aarhus, Institute of Integrated Pest Management.

The compounds were separated with HPLC on a BDS Hypersil C18 column from Thermo Electron Corporation (Waltham, MA) with dimensions of  $250 \times 2.1$  mm and a particle size of  $5 \mu\text{m}$ . The content was measured with mass spectrometry with atmospheric pressure chemical ionization (APCI) in positive SIM mode and masses  $m/z$  252 and  $m/z$  212 for prosulfocarb and pendimethalin, respectively.

The injection volume was  $20 \mu\text{L}$ . The eluents were: (A) 99% 10 mM ammonium acetate and 1% methanol and (B) 90% methanol and 10% 10 mM ammonium acetate. The flow was  $0.5 \text{ mL min}^{-1}$ .

The gradient started with 50% B, and from minute 2 to 8, the gradient changed linearly to 100% B, which was kept for 5 min. From 13 to 15 min, the gradient changed linearly back to initial conditions, which were kept for 5 min to restabilizing the system. The column temperature was  $50^\circ\text{C}$ .

The eventual content in blank matrix was deducted from the analytical results. For the diluted samples, the area was corrected for the matrix effect, and the concentrated samples were corrected for the loss during preconcentration. The content of the active ingredient in the samples was calculated as grams per hectare.

### 3. Results and discussion

#### 3.1 Deposition on target

The theoretical amount in the sprayer tank, the analysis of the tank sample, and the mean amount of active ingredient measured at hour 0 in the field can be seen in table 2, all calculated as grams per hectare.

The analytical results of the tank content were in good agreement with the theoretical content. Table 2 displays the exposure of leaves and soil as a percentage of the spray dose. The measured amount at hour 0 of prosulfocarb and pendimethalin was 66 and 38% on soil and 37 and 24% on cabbage leaves, so a considerable part of the amount of pesticides in the spray solution could not be recovered on the dosimeters. The loss took place from the pesticides leaving the sprayer to the deposition on the dosimeters or by volatilization from application to first sampling, which was a few minutes after spraying. The loss could be caused by drift during the spraying and volatilization of the spraying steam [14].

#### 3.2 Recovery and background samples

Matrix can reduce or enhance the signal in the mass spectrometer, and part of the analytes can be lost during sample preparation. In table 4, the matrix effect is displayed



Table 4. Matrix and recovery samples in per cent of signal of standards.<sup>a</sup>

|                                                   | Prosulfocarb (%)       | Pendimethalin (%)      |
|---------------------------------------------------|------------------------|------------------------|
| Matrix influence leaf sample                      | 120 ± 10               | 130                    |
| Matrix influence soil sample                      | 120 ± 10               | 130 ± 20               |
| Recovery percent, preconcentration of leaf sample | 84 ± 3                 | 76 ± 2                 |
| Recovery percent, preconcentration of soil sample | 83 ± 3                 | 84 ± 5                 |
| Background blank, leaf sample                     | 0.06 ± 0.02            | 0.19 ± 0.10            |
| Background blank, soil sample                     | 0.04 ± 0.00            | 0.81 ± 0.07            |
| Detection limit leaf samples                      | 0.3 µg L <sup>-1</sup> | 0.7 µg L <sup>-1</sup> |
| Detection limit soil samples                      | 0.1 µg L <sup>-1</sup> | 0.1 µg L <sup>-1</sup> |

<sup>a</sup>Background blank samples calculated as percentage values of the content at hour 0 inside spray zone—mean ± SD and detection limits.

as well as the recovery percentage of samples spiked with a known amount of analyte. The matrix influence is determined by spiking the matrix with a known amount of analyte. It appears from table 4 that the matrix enhances the signal, while some analyte is lost during preparation, ending up with recovery percentages of around 80%.

The amount of active ingredient in the blank samples, which were placed upwind of the field, can also be read from table 4. The amount of prosulfocarb was almost the same on leaf and soil surfaces, 0.04–0.06%, whereas the amount of pendimethalin was much higher on soil surfaces than on the cabbage surface, 0.8 and 0.2%. The higher vapour pressure of prosulfocarb could explain the lower deposition rate for prosulfocarb than for pendimethalin, which also was seen on the dosimeters downwind. Many farmers in the region were spraying with these two compounds in the period when the study was performed, and the results indicate that pesticides are applied to soil and plants all over the countryside as secondary deposition. Background samples were exposed from 24 to 27 h after spraying, and all samples were corrected for these background values. From 24 to 27 h after spraying, the period when the figures are correctly adjusted for background, there is a decreasing contribution to the secondary deposition from 5 to 25 m from the spray zone, and still a contribution from the field 25 m away. The ideal background correction would have been background samples during the whole study. However, the pronounced gradient in exposure from 5 to 25 m from the field further demonstrates that exposure is caused by secondary deposition from the field.

### 3.3 Volatilization results

The results of the volatilization from the cabbage surfaces can be seen in figure 6 and from the soil surfaces in figure 7. Data points are provided ±SD as error bars. It is presumed that volatilization is the main way in which the compound is lost from the passive dosimeters compared with degradation during the 48 h of the experiment, since no significant loss is measured from the soil surfaces.

On the cabbage surfaces, 60% of the sprayed amount of pendimethalin and 81% of prosulfocarb were lost during the experiment. The reduction after 48 h is significant, even with the relatively high SDs. On soil, no significant loss of the two compounds could be measured during the 48 h study period. These results support the statement that the dissipation from the leaves is caused by volatilization because eventual

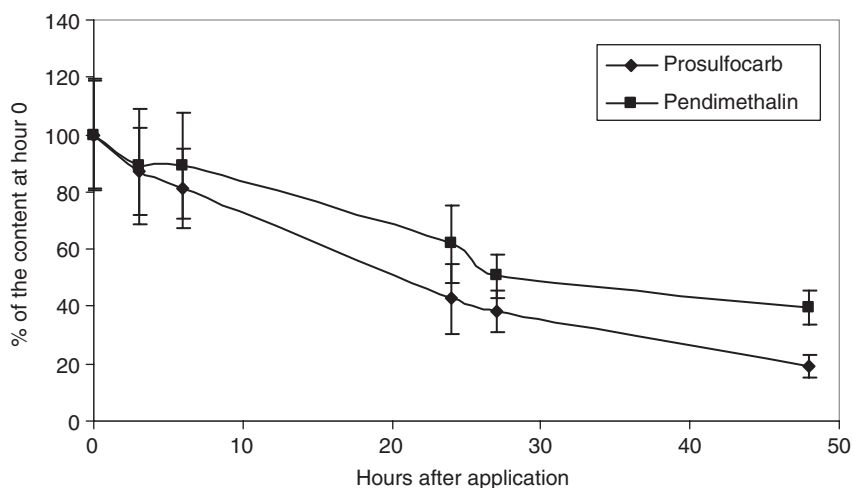


Figure 6. Volatilization from Chinese cabbage surface as percentages of the values measured at hour 0.

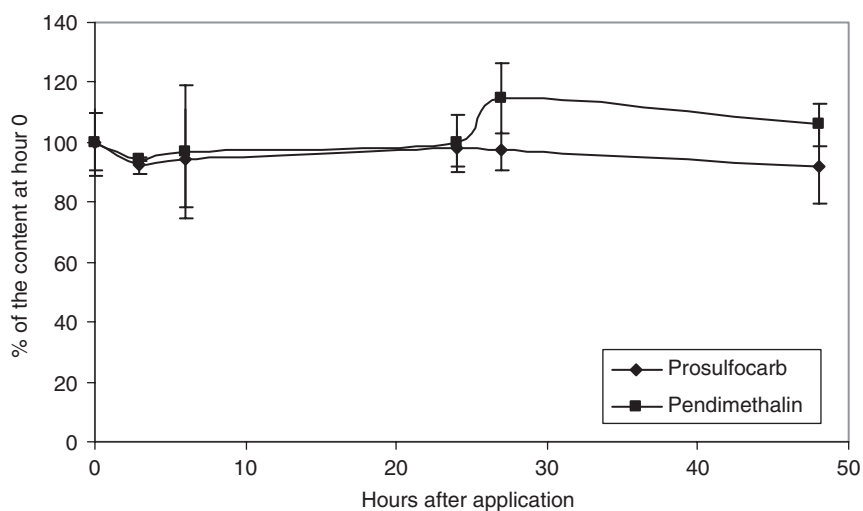


Figure 7. Volatilization from soil surface as percentages of the values measured at hour 0.

photolysis or metabolism from leaves also would have been expected from the soil, which is not the case.

This observation is in good agreement with the higher possibility of adsorption to the soil surface which can reduce the volatilization [11], and the theory of adsorption is in agreement with the Dow method for volatilization of pesticides from plant surfaces where the volatilization is assumed to depend only on the vapour pressure of the active ingredient [16]. The higher volatilization rate of prosulfocarb than of pendimethalin in the present study was in good agreement with the higher vapour pressure (6.9 mPa for prosulfocarb and 1.9 mPa for pendimethalin).

Garcia-Valcarcel and Tadeo [17] measured the influence of organic fertilizer application on pendimethalin volatilization from soil surfaces. Minor differences were

Table 5. Volatilization 24 h after application measured on glass slides by Carlsen *et al.* [13] compared with volatilization in this experiment 24 h after application.<sup>a</sup>

| Compound      | Volatilization from glass slides [13] (%) | Volatilization from cabbage surface (%) | Volatilization from soil surface (%) |
|---------------|-------------------------------------------|-----------------------------------------|--------------------------------------|
| Prosulfocarb  | 80                                        | 60                                      | 2                                    |
| Pendimethalin | 68                                        | 40                                      | 0                                    |

<sup>a</sup>All the values are as a percentage of the sprayed amount.

demonstrated among different applications, but the volatilization after 48 h was in all cases less than 2% of the initial amount, which is in good agreement with the results from the present study, where the volatilization from soil was minimal. The volatilization of prosulfocarb, pendimethalin, bromoxynil octanoate, and ioxynil octanoate from glass slides 24 h after application was measured by Carlsen *et al.* [13], and the results for prosulfocarb and pendimethalin can be seen in table 5 together with the results from hour 24 in this experiment. The volatilization rate was higher from glass slides compared with cabbage and soil.

In a laboratory experiment performed by Pestemer and Krasel [7], 100% of pendimethalin volatilized from cabbage surfaces, and 30% volatilized from aqueous surfaces, after 24 h at 40°C. These volatilization rates were higher than in the present experiment. This could be due to the type of surfaces, the higher temperatures, and the fact that the experiment was performed in a laboratory.

### 3.4 Deposition results

Figure 8 displays the accumulated secondary deposition of the two compounds 5, 10, and 25 m away from the field during the first 48 h after spraying. The deposition was calculated as a percentage of the applied dose on the dosimeters in the spray zone. The volatilization results showed that volatilization from soil was minimal, so the source for secondary deposition was primarily the barley leaves. The deposition on soil and leaves was comparable. At a distance of 5 m, 6% of the prosulfocarb field dose was found on the leaves, while 4% was found on the soil. Pendimethalin was found in higher amounts with 10% on the leaf surfaces and 8% on the soil surfaces. At a distance of 25 m from the spray zone, the deposition was reduced, but still about 2% of the field dose of prosulfocarb and 4% of pendimethalin were found on the dosimeters. The lower findings of prosulfocarb could be explained with the higher vapour pressure, which means a faster secondary volatilization from the dosimeters.

Most of the deposition took place during the first 24 h, but the deposition from 24 to 48 h was still significant on soil surfaces. The accumulated deposition of prosulfocarb on soil increased from 3 to 4% 5 m away from 24 to 48 h, and the deposition of pendimethalin increased from 6 to 8%. The deposition on leaves after 24 h was less pronounced.

Siebers *et al.* [18] investigated the deposition of volatilized lindane and parathion on water surfaces and found that lindane as the most volatile and most persistent of the investigated active compounds showed the highest entries in surface water with 35 and 153  $\mu\text{g m}^{-2}$  after 1 day at a distance of 10 m, giving a greater deposition than spray drift.

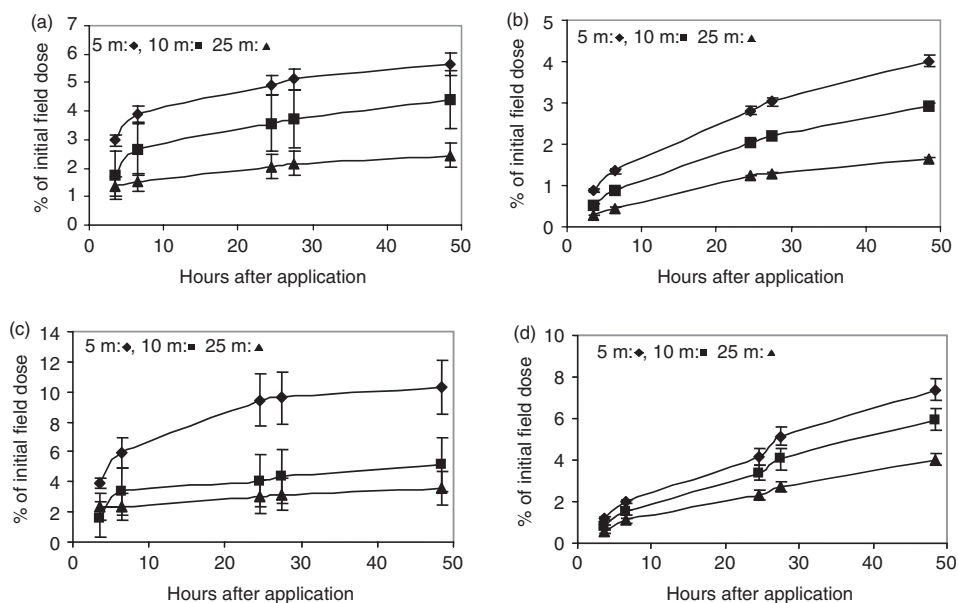


Figure 8. Accumulation of secondary deposition outside the spray zone of the two compounds. (a) Prosulfocarb on leaf surface. (b) Prosulfocarb on soil surface. (c). Pendimethalin on leaf surface. (d) Pendimethalin on soil surface.

Table 6. Accumulated deposition ( $\text{g ha}^{-1}$ ) of prosulfocarb and pendimethalin 5, 10, and 25 m away from the spray zone 48 h after spraying.

|            | Prosulfocarb ( $\text{g ha}^{-1}$ ) | Pendimethalin ( $\text{g ha}^{-1}$ ) |
|------------|-------------------------------------|--------------------------------------|
| Leaf, 5 m  | 25                                  | 3.8                                  |
| Leaf, 10 m | 19                                  | 1.9                                  |
| Leaf, 25 m | 11                                  | 1.3                                  |
| Soil, 5 m  | 32                                  | 4.3                                  |
| Soil, 10 m | 23                                  | 3.4                                  |
| Soil, 25 m | 13                                  | 2.3                                  |

The vapour pressure of lindane is 5.6 mPa at 20°C and comparable with the vapour pressures of the compounds used in the present study. Table 6 shows the accumulated deposition after 48 h in the present study. At a distance of 10 m, the deposition was in the range of 367–2478  $\mu\text{g m}^{-2}$ . The present setup with soils and leaves as receptors gave deposition rates which were 10 to 16 times higher than the setup with water surface as receptor.

The results of this study were compared with primary deposition results from former studies, since there are no secondary deposition results in the literature for the investigated compounds.

The deposition of prosulfocarb decreased from 5 to 10 and to 25 m on both soil and cabbage surfaces, and the decrease was significant from 5 to 25 m. The total deposition on cabbage and soil surfaces, respectively, was almost the same at each distance, which implies that none of the surfaces was markedly better as a collecting material.

The primary deposition of prosulfocarb has been measured in a former study at the edge of the sprayed field to 30% of the sprayed amount and 17 m from the spray

zone to 0.75% of the sprayed amount immediately after spraying [19]. The primary as well as the secondary deposition of prosulfocarb decreased as the distance to the sprayed field increased, but the decrease in primary deposition was much more pronounced.

The deposition of pendimethalin on cabbage surfaces was significantly different at 5 and 25 m. On soil surfaces, the deposition at 25 m was significantly lower than the deposition at 10 m. On the cabbage surface, stagnation was observed from hour 24.5 to 48.5 after application. This could be explained by the equilibrium between deposition and re-volatilization [20]. On soil surfaces, the deposition increased through the entire experiment. Here, the deposition was greater than the re-volatilization.

Rautmann *et al.* [21] used results from 50 agricultural drift trials to construct a power function, which was suitable as an equation for the estimation of primary drift in field crops. The equation was expressed as  $y = 2.7705x^{-0.9787}$ , where  $y$  is ground sedimentation as a percentage of the application rate, and  $x$  is the distance in metres from the treated area. In a previous study [19], the equation was compared with our own experimental results, and we obtained a reasonable agreement with the Rautmann equation. Using this equation, the primary deposition rates were calculated as 0.6, 0.3, and 0.12%, 5, 10, and 25 m away from the field. In figure 9, the deposition is shown as a

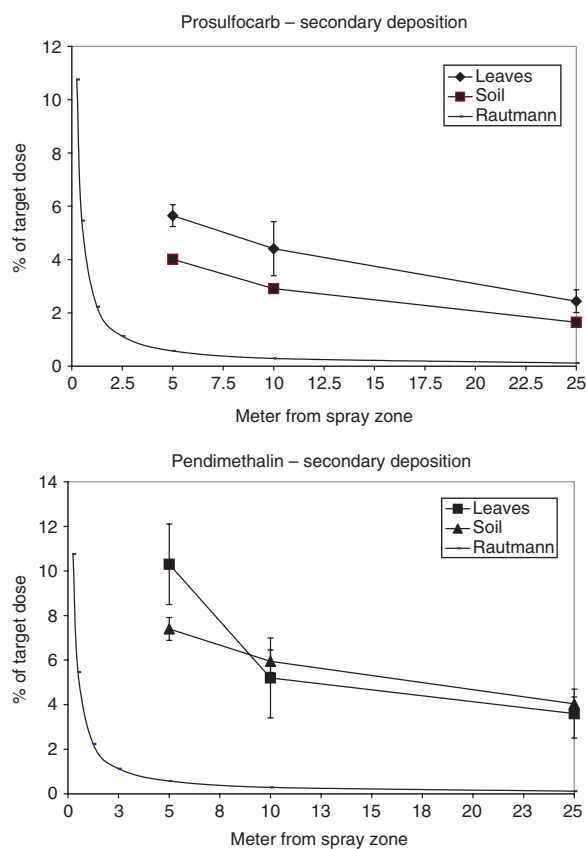


Figure 9. Secondary deposition of pendimethalin and prosulfocarb as a percentage of target dose at three different distances from the field. The Rautmann equation gives an estimation of the primary deposition.

Table 7. Primary deposition measured by Carlsen *et al.* [19] 1 h after application on dosimeters with glass slides, and the secondary deposition measured 3 h after application 25 m from the spray zone.

| Compound          | Primary deposition<br>3 m away from<br>spray zone [20] (%) | Primary deposition<br>25 m away from<br>spray zone [20] (%) | Secondary deposition<br>25 m away from<br>spray zone—leaf<br>surface (%) | Secondary deposition<br>25 m away from<br>spray zone—soil<br>surface (%) |
|-------------------|------------------------------------------------------------|-------------------------------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Prosulfocarb      | 0.05–0.12                                                  | 0.04                                                        | 1.3                                                                      | 0.3                                                                      |
| Pendimethalin     | 0.10–0.35                                                  | 0.05–0.15                                                   | 2.3                                                                      | 0.6                                                                      |
| Rautmann equation | 0.95                                                       | 0.12                                                        |                                                                          |                                                                          |

<sup>a</sup>Values are given as a percentage of the applied amount. The Rautmann equation figures are given for comparison.

function of distance. The Rautmann equation is depicted in the figure giving an estimation of the primary deposition. The predominant method of deposition was secondary deposition when the distance was more than 0.5 m away from the spray zone. The secondary deposition declined at a slow rate, going from 5 to 25 m, and was only reduced by a factor 2, while the primary deposition was reduced by a factor of 5.

The primary deposition of prosulfocarb and pendimethalin was measured using passive dosimeters with glass slides as collective material 1 h after spraying [19], which is displayed in table 7 where the secondary deposition measured in this experiment and the Rautmann equation are also shown for comparison. For both compounds, the secondary deposition was higher both near and far away from the sprayed field, when the results 3.5 h after spraying were compared with the survey of primary deposition. This implies that the secondary deposition is an important source of pesticide exposure in areas near the sprayed zone.

### 3.5 Soil and cabbage leaves as collective material

The exposure of the dosimeters in the spray zone was measured shortly after the spraying (about 30 min). The spraying direction was vertically directly towards the dosimeters, and the soil surfaces gave 58–78% higher doses than the leaf surfaces. A higher adsorption was expected to the soil surface compared with the adsorption ability of the cabbage surface [16], and for prosulfocarb as well as for pendimethalin, a higher volatilization rate was observed from the cabbage surface compared with the soil surface, as expected. Regarding secondary deposition, it was expected that the deposition would be higher on soil surfaces as well, since the active ingredients could adsorb to soil particles and re-volatilization thereby was reduced [8]. This theory did not fit the results. For both compounds, it was found that the secondary deposition was higher on leaf surfaces than on soil surfaces. The transport from the spray zone to the dosimeters outside the spray zone is diffuse, and the edge of the Petri dish with soil might act as a barrier for contact when the movement is lateral while there was no edge on the leaf dosimeter, which could act as barrier.

## 4. Conclusion

Passive dosimeters were tested for determination of volatilization, measured as dissipation and secondary deposition. The volatilization rates from leaves and soil were measured for prosulfocarb and pendimethalin, which are pesticides with relatively

high vapour pressures, and the volatilization of both compounds was pronounced with losses of 80 and 60% from leaves after 48 h. Prosulfocarb, which had the highest vapour pressure, gave the highest volatilization rate, as expected. No volatilization was seen from soil, which indicates that the dissipation from leaves was caused by volatilization. The secondary deposition caused by volatilization from the field of the two pesticides prosulfocarb and pendimethalin was pronounced and made a much higher contribution to the total deposition than the contribution from the primary spray drift estimated from the Rautmann equation. The Rautmann equation estimates the primary deposition to 0.6 and 0.1% of field dose at a distance of 5 and 25 m. At a distance of 5 m from the field, 6% of the field dose of prosulfocarb was measured on dosimeters with China cabbage leaves, while 10% of the pendimethalin field dose could be measured. At a distance of 25 m, the accumulated deposition was 2 and 4% for the two compounds. The deposition on the soil was in the same order of magnitude but slightly less pronounced. The study demonstrated the importance of taking the deposition caused by volatilization and secondary drift into account when border zones are stipulated for the use of pesticides with relatively high vapour pressures.

## References

- [1] C. Bedos, P. Cellier, R. Calvet, E. Barriuso. *Agronomie*, **22**, 35 (2002).
- [2] R. Bossi, K.V. Vejrup, B.B. Mogensen, W.A.H. Asman. *J. Chromatogr. A*, **957**, 27 (2002).
- [3] W.A.H. Asman, A. Jørgensen, R. Bossi, K.V. Vejrup, B.B. Mogensen, M. Glasius. *Chemosphere*, **59**, 1023 (2005).
- [4] J. Kreuger, M. Törnquist, H. Kylin. *Swedish University of Agricultural Sciences Ecohydrologi*, **81**, 18 (2004).
- [5] R. Huskes, K. Levsen. *Chemosphere*, **35**, 3013 (1997).
- [6] J.R. Plimmer. *Am. J. Ind. Med.*, **18**, 461 (1990).
- [7] W. Pestemer, G. Krasel. *Brighton Crop Protection Conference—Pests and Diseases*, **6**, 459 (1992).
- [8] C. Bedos, P. Cellier, R. Calvet, E. Barriuso, B. Gabrielle. *Agronomie*, **22**, 21 (2002).
- [9] H. Rüdél, B. Waymann. *Brighton Crop Protection Conference—Pests and Diseases*, **2**, 841 (1992).
- [10] H. Rüdél. *Chemosphere*, **35**, 143 (1997).
- [11] F. Van Den Berg, R. Kubiak, G.W. Benjey, M.S. Majewski, S.R. Yates, G.L. Reeves, J.H. Smelt, A.M.A. Van Der Linden. *Water Air Soil Pollut.*, **115**, 95 (1999).
- [12] M.S. Majewski. *Water Air Soil Pollut.*, **115**, 83 (1999).
- [13] S. Carlsen, N.H. Spliid, B. Svensmark. *Chemosphere*, **64**, 787 (2006).
- [14] C.M. Himmel, H. Loats, G.W. Bailey. In *Pesticides in the Soil Environment: Processes, Impact, and Modeling*, H.H. Cheng (Ed.), Chapter 2, Soil Science Society of America, Madison, WI (1990).
- [15] J. Epple, J. Maguhn, P. Spitzauer, A. Kettrup. *Geoderma*, **105**, 327 (2002).
- [16] J.W. Jansma, J.B.H.J. Linders. *Volatilization of Pesticides from Soil and Plants After Spraying*, National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands (1995).
- [17] A.I. Garcia-Valcarcel, J.L. Tadeo. *J. Agric. Food Chem.*, **51**, 999 (2003).
- [18] J. Siebers, R. Binner, K. Wittich. *Chemosphere*, **51**, 397 (2003).
- [19] S. Carlsen, N.H. Spliid, B. Svensmark. *Chemosphere*, **64**, 778 (2005).
- [20] J.v. Jaarsveld, W.A.J. van Pul. *Water Air Soil Pollut.*, **115**, 167 (1999).
- [21] D. Rautmann, M. Streløke, R. Winkler. *Workshop on Risk Assessment and Risk Mitigation Measures in the Context of Authorization of Plant Protection (WORMM)*, R. Forster, M. Streløke (Eds), Vol. 383, pp. 133–141, Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft Berlin-Dahlem (2001).
- [22] C.D.S. Tomlin. *The e-Pesticide Manual ver. 3.2*, BCPC, 2005–2006.