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**Adsorption, transformation and leaching of the insecticide  
pirimicarb in orchard soils**

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## ABSTRACT

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The risk of leaching of pirimicarb to groundwater after its use for insect control in integrated fruit production had to be evaluated. The adsorption of pirimicarb onto loamy soils is moderate and its half-life at 15 °C is around 53 days. With a model simulating uniform water flow and equilibrium adsorption, the concentration leaching to the upper groundwater was estimated to be 0.01 µg/L or less. In a leaching study with soil columns in the laboratory, a small fraction of the insecticide was leached quickly, whereas the main part of the concentration pattern moved much less than expected.

Keywords: fruit growing, groundwater, pesticide, chemical analysis, residues.

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## PREFACE

This research was carried out within the framework of the project "Leaching of pesticides used in some systems of fruit growing". The work was co-ordinated by the Working Group Integrated Fruit Production. The Research Station for Fruit Growing, Wilhelminadorp, provided financial support for the study. Mrs E. Romero Taboada from Granada, Spain, participated in this research project during her stay at the DLO Winand Staring Centre in the period from November 1990 to November 1991. Thanks are due to W.H.J. Beltman and R.Ch. Sjardijn for their advices with respect to the experiments and analyses.

## SUMMARY

Pirimicarb is a selective insecticide that can be used in integrated fruit growing systems. If some use of pesticides is necessary in such systems, it is preferred to use compounds with minimal risks to the environment. In this framework, the risk of leaching of pirimicarb to groundwater, after its application to fruit orchards, had to be studied.

There was a lack of basic data on the behaviour of pirimicarb in soil. Soil batches were collected from the experimental fruit farms in Numansdorp and Zeewolde and the adsorption and transformation of pirimicarb in these soils were measured. Columns of the loamy soils were taken at the experimental farms to study the leaching of pirimicarb in the laboratory. Bromide-ion was used as tracer for water flow in the columns.

Pirimicarb in water and in soil extracts was analysed with two systems of liquid chromatography, using spectrophotometric UV-detection. A pre-concentration procedure was developed to analyse the low concentrations of pirimicarb. At the lowest concentrations in the soil extracts, there was some interference by co-extracted compounds.

The adsorption coefficients  $K_d$  of 1.3 and 2.4 dm<sup>3</sup>/kg measured for the Numansdorp and Zeewolde soils, respectively, point to moderate adsorption of pirimicarb onto the loamy soils. They allow a more narrow range in the first estimate of the leaching of pirimicarb from soils than the wide range of adsorption coefficients reported in the literature.

Approximation of the adsorption data with the Freundlich equation yields values of the Freundlich exponent distinctly below 1.0. This means that there is a substantial curvature in the adsorption isotherm. If such a curvature is introduced into computations, a distinctly lower leaching is computed than with the approximate linear adsorption isotherm.

In the incubation period of 49 days at 15 °C, pirimicarb was transformed in the soils to about half of its initial amount. There was a comparatively fast transformation in the first few days. The calculated half-lives of pirimicarb were 55 days (Numansdorp) and 51 days (Zeewolde).

On the basis of the adsorption coefficients and the transformation rate coefficients measured in the present study, a first estimate can be made of the leaching of pirimicarb from orchard soils to the upper groundwater. The results of computer-simulations for hypothetical pesticides applied to a loamy soil in spring were used for the estimates. For the dosage of 0.6 kg/ha of pirimicarb in current fruit growing, the estimated concentration leaching from the Numansdorp soil is 0.01 µg/L. The reduced dosage used in integrated fruit growing results in the first estimate of the leaching concentration to be half of this.

For the Zeewolde soil, the first estimate of the leaching concentration in current fruit growing is less than 0.001 µg/L and for the reduced dosage in integrated fruit growing it is even lower. The difference in estimated leaching concentration for the two soils is caused by the combination of stronger adsorption and faster transformation in the Zeewolde soil.

In the first estimate of leaching, it is assumed that the full dosage of pirimicarb penetrates into the soil. However, only a small fraction of the dosage (directed to the fruit trees) is expected to penetrate into the soil because of interception, volatilization and photochemical transformation. A second estimate accounting for the actual load of the soil system with pirimicarb will lead to distinctly lower leaching concentrations.

By using bromide-ion as a tracer for water flow in the soil column leaching experiment, it was found that a fraction of the water flows much faster than expected from uniform water flow. On the other hand, the tailing in the effluent curve showed that a fraction of the bromide-ion had diffused into more stagnant regions of the soil water phase. It took some time for the bromide-ion to diffuse back to the more mobile regions in the water phase.

After the total irrigation corresponding to 0.54 m water layer had been applied to the soil columns (in 24 irrigation days), the peak of the concentration pattern of pirimicarb was still in the top of the soil columns. The movement of this peak was much less than expected on the basis of the adsorption coefficients. On the other hand, a small fraction of the pesticide appeared very soon in the effluent. The amount of pirimicarb leaching from the Numansdorp and Zeewolde soil columns (about 0.24 m long) was estimated to be 6.5% and 3.5% of the dosage, respectively.

The estimates show that a computation model simulating uniform water flow and instantaneous adsorption-desorption equilibration is not suitable for describing the movement of a pesticide like pirimicarb in structured loamy soils at relatively high flow rates of water. On the one hand, an improved computation model should describe the comparatively fast transport of a small fraction of a pesticide distribution with highly mobile water. On the other hand, it should describe the slow release of pesticide from the soil regions with a more stagnant water phase, containing much of the adsorbing surfaces.

## 1 INTRODUCTION

Pirimicarb is a selective insecticide used for the control of noxious aphid species in arable crops, vegetables, fruit crops and ornamentals. Its chemical name is 2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate. It can be applied in integrated crop protection programs, because it is relatively non-toxic to beneficial insects such as honey bees and predators of pest organisms. The application rate of pirimicarb in current fruit growing is about 0.3 kg active ingredient (a.i.) per hectare and this rate may be applied two times in a growing season.

In integrated fruit production, the use of pesticides is restricted as much as possible. Further, it is preferred to use pesticides which present minimal risks to the environment. In this context, information was needed on the risk of leaching of pirimicarb to groundwater when used in fruit orchards. Attempts are being made to restrict the use of pirimicarb in fruit growing to less than two times 0.17 kg a.i. per hectare in a growing season.

In an inventory study on the risk of leaching of six pesticides used in fruit growing (van der Kolk & Leistra, 1990) it was concluded that there is a possible risk of leaching of pirimicarb to groundwater. The concentration in shallow groundwater could exceed the EC limit value for pesticides in drinking water (0.1 µg/L). The estimates on the leaching were made using the results of computations with the model PESTLA, developed by Boesten & van der Linden (1991). The risk of leaching from a loamy soil was estimated by computations to be less than that of leaching from a humic sandy soil. However, these estimates suffered from a lack of adequate basic data on pirimicarb behaviour in soils, that are needed as input data for such leaching models. Main characteristics with respect to the leaching of pesticides through soils are their extent of adsorption and their rate of transformation in the soils.

A review of the published information on the physico-chemical properties of pirimicarb and its interactions with soils has been given by Leistra (1992). Data are available on the adsorption of pirimicarb onto various Spanish soils (Sanchez-Camazano & Sanchez-Martin, 1988). The content and nature of the clay minerals in the soils seem to be important for the extent of adsorption, so it was not easy to translate these data to other soils. Only very few data have been published on the rate of transformation of pirimicarb in soils (Leistra, 1992). The leaching behaviour of a pesticide may be expected to be also dependent on soil structure condition and water regime.

In this study, the adsorption of pirimicarb onto two orchard soils was measured (Chapters 2.2 and 3.1). The rate of transformation of the insecticide in the two soils was measured in an incubation study (Chapters 2.3 and 3.2). The leaching in the orchard soils was studied in the laboratory with soil columns, provided with a rainfall simulator (Chapters 2.4 and 3.3). The water flow in the columns was characterized by using bromide-ion as a tracer. The leaching of bromide-ion was simulated with a computation model. The measured movement of pirimicarb in the soil columns is compared with the movement expected on the basis of the adsorption coefficients.

## 2 MATERIALS AND METHODS

### 2.1 Description of the soils

The soils were collected at the experimental fields for integrated fruit production of the experimental fruit farms at Numansdorp (province of South-Holland) and Zeewolde (province of Flevoland). The soil batches for the adsorption and transformation studies were taken with an auger from the top 0.2 m layer and they were sieved and mixed. The soil columns were taken with poly(methacrylate) cylinders, provided with a steel cutting ring at the bottom end. The characteristics of the soils are given in Table 1.

*Table 1 Characteristics of the soils (top 0.2 m) taken from the experimental fruit farms in Numansdorp and Zeewolde. Measured by the Laboratory for Soil and Crop Testing in Oosterbeek, The Netherlands*

Soil	Numansdorp	Zeewolde
Clay (< 2 µm; %)	29.4	36.7
Silt (2 to 50 µm; %)	43.3	51.5
Textural class	clay loam	silty clay loam
Organic matter (%)	1.8	2.0
CaCO <sub>3</sub> (%)	8.5	8.8
Cation exchange capacity (meq/kg)	195	242
pH-KCl	7.3	7.2

### 2.2 Adsorption measurements

The adsorption of pirimicarb was measured for the 0 to 0.1 m and 0.1 to 0.2 m layers of both soils. Solutions of pirimicarb in water (with 0.01 mol CaCl<sub>2</sub> per litre) were made at concentrations of 0.1, 1.0 and 10 µg/mL. A volume of 20 mL of the solution was added to 5 g of moist soil in glass centrifuge tubes (50 mL) with ground-glass stoppers. The tubes were shaken (end-over-end) for 24 hours at 20 °C in the dark. After centrifugation, a fraction of the solution was filtered and analyzed by liquid chromatography. The adsorption of pirimicarb was calculated from the difference between the initial and final concentrations in solution. The measurement at each concentration was carried out in duplicate. Soil-solution combinations without pirimicarb were processed in the same way; no compounds interfering with the chemical analysis showed up in the solution.

The adsorption of pirimicarb onto the soils is described first of all with the linear adsorption equation:

$$X = K_d C \quad (1)$$

with:  $X$  = the content adsorbed (mg/kg);  
 $K_d$  = the adsorption coefficient (dm<sup>3</sup>/kg);  
 $C$  = the concentration in solution (mg/dm<sup>3</sup>).

Secondly, the adsorption of pirimicarb onto the soils is described with the Freundlich equation:

$$X = K_f C_{ref} (C/C_{ref})^n \quad (2)$$

with:  $K_f$  = the Freundlich coefficient (dm<sup>3</sup>/kg);  
 $C_{ref}$  = a reference concentration in solution (mg/dm<sup>3</sup>);  
 $n$  = the Freundlich exponent (-).

This equation takes the non-linearity of the adsorption isotherm into account. The Freundlich equation was fitted to the measurements using linear regression analysis.

It may be attempted to express the adsorption onto soils on the basis of their organic matter content:

$$K_{om} = K_d/omc \quad (3)$$

with:  $K_{om}$  = adsorption coefficient based on soil organic matter (dm<sup>3</sup>/kg);  
 $omc$  = soil organic matter content (kg/kg).

The values of  $K_{om}$  for the two soils are compared.

### 2.3 Incubation experiment

The rate of transformation of pirimicarb in the two soils was measured in an incubation experiment. The moisture contents of the soils were 20% (Numansdorp) and 25% (Zeewolde). For each soil, two series of eleven glass bottles (250 mL) were provided with 60 g moist soil. The soils were pre-incubated for seven days at 15 °C. A solution of pirimicarb in water of 130 µg/mL was made and 1 mL of this solution was added with a syringe to the soil in the bottles. Subsequently, the contents of the bottles were mixed. So the initial content of pirimicarb was about 2.60 µg/g (on dry soil basis) in the Numansdorp soil and it was 2.71 µg/g in the Zeewolde soil. The bottles were covered with aluminium foil, provided with a small hole to keep the conditions aerobic. The bottles were placed at 15 °C in the dark. After incubation periods of 0, 1, 2, 3, 7, 14, 21, 30, 35, 42 and 49 days one bottle of each series (two per soil) were frozen to - 20 °C to stop the transformation.

Shortly before the extraction, the bottle contents were defrosted. Pirimicarb was extracted from the soils with acetonitrile/water (containing 0.01 mol CaCl<sub>2</sub> per litre) at the ratio 1/1. The bottle contents were extracted with 100 mL extraction liquid by

shaking for 1 hour on a reciprocating shaker, which was followed by vibration for 10 min in an ultrasonic bath. The soil and liquid layers were separated by centrifugation for 10 min and a subsample of about 5 mL of the liquid layer was filtered before it was placed in the autosampler of the liquid chromatograph. Because the contents of pirimicarb in this experiment were comparatively high, there was little effect of interfering substances in the analysis.

Attempts can be made to describe the course of the transformation in time with the first-order rate equation:

$$R_t = k_r C_s \quad (4)$$

with:  $R_t$  = rate of transformation ( $\text{mg}/(\text{dm}^3 \text{ d})$ );  
 $k_r$  = first-order rate coefficient ( $1/\text{d}$ );  
 $C_s$  = concentration in soil ( $\text{mg}/\text{dm}^3$ ).

#### 2.4 Leaching experiment with soil columns

Two soil columns (about 0.24 m long) were taken on each field with poly(methacrylate) cylinders (0.4 m long; 0.12 m inner diameter). The cylinders were provided with a screwed-on steel cutting ring (inner diam. 0.108 m) and they were hammered into the soil.

In the laboratory, a sand filter (0.03 m thick) was prepared to facilitate the flow of water from the columns. The washed sand graded from coarse sand (around 0.85 mm) at the bottom to very fine sand (around 0.075 mm) on the top. The filters contained in filter pieces were water-saturated and then frozen. The cylinders with the soil columns were turned in horizontal position to remove the steel cutting ring and to attach the frozen filter piece tightly with screwed-on ring and bolts. The filter piece was provided with an outlet tube for the collection of the percolation water.

The leaching experiment was carried out with two columns for each soil. The top layer (0.05 m) was removed from the column and then replaced, to avoid large cracks at the soil surface. A layer of 0.01 m of coarse sand was placed on top of the columns. The cylinders were wrapped in aluminium foil to prevent photochemical transformation due to exposure to light. They were placed at 18 °C in a laboratory in the basement.

A rainfall simulator was placed on top of the cylinders. It consisted of a disc pierced downward by 26 syringe needles. The syringe tubes were cut-off so that a volume of 3.5 mL could be retained. After filling, this volume dripped slowly onto the surface of the soil column. The syringes were equally distributed over the surface area of the column. Three simulated-rainfall cycles were applied per day. Prior to the experiment, water was applied for a few days until steady-state water flow (on a daily basis) occurred in the columns. At zero time 10 mL of pirimicarb solution in water with a concentration of 100  $\mu\text{g}/\text{mL}$  was evenly distributed with a syringe over the surface of

the soil columns. This corresponds to an application rate of 0.88 kg/ha in the field. Subsequently, another 0.01 m layer of coarse sand was placed on top of the columns to reduce possible volatilization. The daily water layer given with the three rainfall cycles was 23 mm.

Bromide-ion was used as a tracer to characterize water flow in the soil columns. Six days after the application of pirimicarb, the supply of bromide-ion was started and it was continued for seven days. The feed concentration of  $\text{CaBr}_2$  in water was 0.01 mmol/mL.

On 24 days in a period of a month the columns were irrigated and the effluent from the columns was collected. The volume of effluent was recorded and the effluent was frozen until the analysis of pirimicarb. In the second and third week of the experiment, a fraction of the effluent samples was set aside for the analysis of bromide-ion.

At the end of the leaching experiment, the soil columns were separated into layers of 0.02 m thickness and the mass of wet soil per layer was determined. Sub-samples of the layers were extracted with acetonitrile/water (with 0.01 mol  $\text{CaCl}_2$  per litre) in the ratio 1/1. For each soil layer, two sub-samples of 25 g were extracted, each with 50 mL extraction solution, by shaking on a reciprocating shaker for 1 hour. This was followed by vibration for 10 min in an ultrasonic bath. The mixture was centrifuged, after which about 5 mL of the extract solution was filtered before the analysis by liquid chromatography. Especially at the lower pirimicarb contents in the soil layers, there was distinct interference by co-extracted compounds in the analysis.

Soil moisture content in the layers was determined by drying sub-samples at 105 °C to constant mass. From the wet and dry masses the dry bulk density of the soil and the volume fraction of water in the layers could be calculated. A survey of the characteristics of the leaching experiment with the soil columns is given in Table 2.

*Table 2 Characteristics of the leaching experiment with the soil columns from Numansdorp and Zeewolde*

	Numansdorp	Zeewolde
Column length (m)	0.25	0.24
Surface area of column (m <sup>2</sup> )	0.0113	0.0113
Soil bulk density (kg/m <sup>3</sup> )	1160	1070
Volume fraction of water (m <sup>3</sup> /m <sup>3</sup> )	0.35	0.39
Water flux density (m <sup>3</sup> /(m <sup>2</sup> d))	0.0228	0.0223
Total irrigation (m)	0.546	0.534

The transport of water-tracer bromide-ion in the soil columns was simulated with a computation model. Starting point was the model PESTLA for the leaching and accumulation of pesticides in soil, described by Boesten & van der Linden (1991). Various simplifications could be introduced into the model to simulate the leaching of bromide-ion in the soil columns, such as:

- steady-state water flow at constant soil water contents;
- no adsorption and no transformation of bromide-ion.

The characteristics of the leaching experiment as given in Table 2 were introduced into the computations.

The measured movement of pirimicarb in the soil columns can be compared with the movement expected on the basis of the adsorption coefficients. The average movement of the insecticide can be estimated with:

$$z_a = V_e / (\epsilon_1 + \rho_b K_d) \quad (5)$$

with:  $z_a$  = average distance of movement (m);  
 $V_e$  = water layer of effluent (m);  
 $\epsilon_1$  = volume fraction of the water phase ( $\text{m}^3/\text{m}^3$ );  
 $\rho_b$  = soil bulk density ( $\text{kg}/\text{m}^3$ ).

The calculated and measured positions of the peak of the distribution of pirimicarb in soil are compared with this equation.

## 2.5 Chemical analysis of pirimicarb

The concentrations of pirimicarb in the water samples and in the extracts from soil were measured by liquid chromatography, using Methods 1 and 2. In all cases, a subsample of about 5 mL was filtered (0.45  $\mu\text{m}$ , Millipore) to remove the fine particles that would block the systems.

The comparatively high concentrations for the adsorption experiment were measured by Method 1, using an SP8000 liquid chromatograph (Spectra Physics). A volume of 100  $\mu\text{L}$  of the water sample was injected with an autosampler (WISP 710; Waters Associates) into the analytical C18 column (Lichrospher 100 RP-18; length 125 mm; inner diam. 4 mm; Merck). The mobile phase of acetonitrile/water (ratio 1/1) was pumped with an SP8800 pump (Spectra Physics) through the column at a flow rate of 1 mL/min. The column-oven temperature was set at 40  $^\circ\text{C}$ . Pirimicarb was detected with a variable-wavelength spectrophotometric UV-detector (LC 90; Perkin Elmer) at a wavelength of 245 nm. Regularly, standard solutions were injected, so the unknown concentrations could be calculated from the calibration line. The retention time of pirimicarb in this system was 4 min. The detection limit for the injected solution was 0.01  $\mu\text{g}/\text{mL}$ .

The extracts from the soils (incubation and leaching experiments) were measured by liquid chromatography using Method 2. A volume of 100  $\mu\text{L}$  of the filtered extract was injected with an autosampler (ISS-100; Perkin Elmer) on a C18 pre-concentration column (Spheri 10 RP-18, length 30 mm; inner diam. 4.6 mm; Brownlee). The mobile phase in this column was water, pumped at a flow rate of 2 mL/min (pump Model 590; Waters). After 3 min, pirimicarb was flushed from the pre-concentration column into the C18 analytical column (Lichrospher 100 RP-18; length 125 mm; inner diam. 4 mm; Merck) mounted in the column oven at 40  $^\circ\text{C}$ . The mobile phase was acetonitrile/water/methanol (10/45/45) and it was pumped at a flow rate of 1 mL/min

(Series 410 LC pump; Perkin Elmer). Pirimicarb was measured with a diode-array detector (LC-235; Perkin Elmer) at a wavelength of 245 nm. The retention time of pirimicarb in the analytical column was 6 min and in the whole system it was 9 min. The detection limit for the soil extracts was 0.01 µg/mL. However, at such very low concentrations there was a distinct interference by other compounds extracted.

The pre-concentration column was re-conditioned by flushing acetonitrile in opposite direction (at 2 mL/min) to remove non-polar compounds. At the same time, the frit was cleaned from blocking particles slipped through the filter. The column was re-conditioned for 9 min with water at a flow rate of 2 mL/min. Further details on liquid chromatography Method 2 have been given by Dekker et al. (1990).

The concentrations of pirimicarb in the effluent of the soil column experiments were also measured with Method 2. Because the concentrations were comparatively low, a much higher volume of 1000 µL of these samples was injected. The detection limit for the soil column effluent concentration was 0.001 µg/mL. However, at this very low level there was some interference by other compounds in the effluent. At the somewhat higher concentrations, around 0.01 µg/mL and higher, such interference was small.

## 2.6 Chemical analysis of bromide-ion

A subsample of the effluent of the soil columns was filtered (0.45 µm; Millipore) and then diluted by a factor ten. The concentration of bromide-ion in water was measured with a liquid chromatograph (Varian 5000) using Method 3. The samples were injected into an analytical column containing the ion-exchanger Ionosphere A (length 100 mm; inner diam. 3 mm; Chrompack). The mobile phase was water, adjusted to pH 3.0 with phosphate buffer to pH 3.0, and its flow rate was 0.4 mL/min. Bromide-ion was detected with a UV detector at a wavelength of 210 nm. The retention time of bromide-ion in this system was 3.5 min. Regularly, standard solutions were injected for making the calibration curve. Further details on this method were given by Harmsen (1982).

### 3 RESULTS AND DISCUSSION

#### 3.1 Adsorption onto the soils

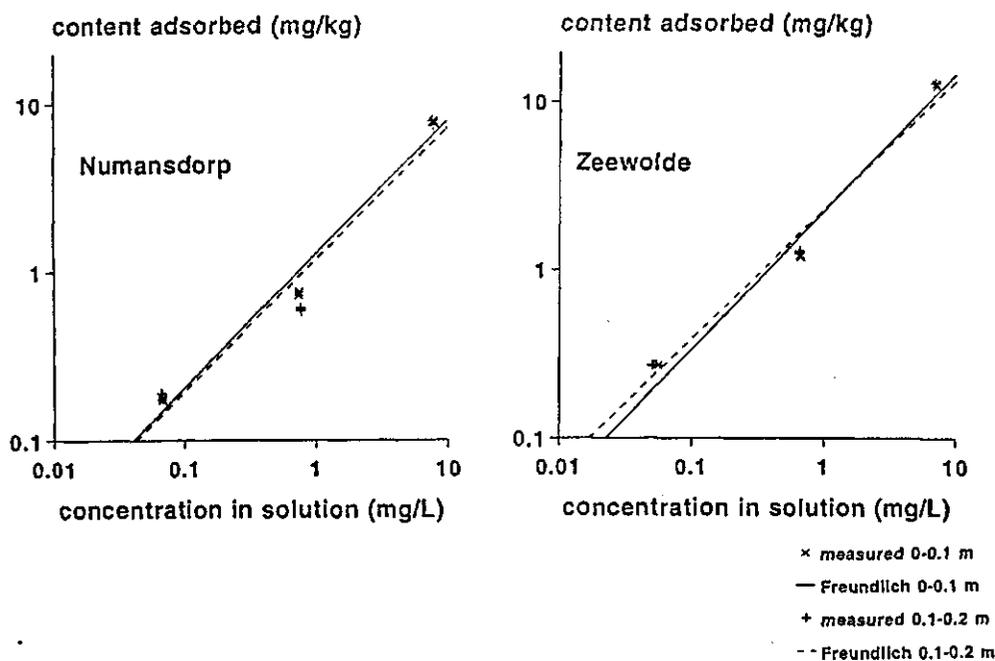
The results of the measurements on the adsorption of pirimicarb onto the soils of Numansdorp en Zeewolde are given in Table 3. The value of the coefficient for linear adsorption,  $K_d$  (Eq. 1), shows that the adsorption is moderate. The two layers of each soil show almost the same extent of adsorption. The adsorption onto the Zeewolde soil is stronger than that onto the Numansdorp soil. This may be related to the higher clay content in the Zeewolde soil (Table 1).

**Table 3** *Coefficients for the adsorption of pirimicarb onto the soils of Numansdorp and Zeewolde*

	Numansdorp		Zeewolde	
	0-0.1 m	0.1-0.2 m	0-0.1 m	0.1-0.2 m
Linear coefficient, $K_d$ ( $\text{dm}^3/\text{kg}$ )	1.29	1.26	2.26	2.47
Freundlich coefficient, $K_f$ ( $\text{dm}^3/\text{kg}$ )	1.27	1.19	2.22	2.29
Freundlich exponent, $n$ (-)	0.79	0.78	0.82	0.77

The adsorption coefficient  $K_{om}$  on the basis of soil organic matter content (Eq. 3) is  $71 \text{ dm}^3/\text{kg}$  for the Numansdorp soil and  $119 \text{ dm}^3/\text{kg}$  for the Zeewolde soil. The difference between the  $K_{om}$  values is rather great. Because content and nature of the clay minerals in soils play a dominant part in the adsorption of pirimicarb (Leistra, 1992), prediction of the adsorption by soils on the basis of  $K_{om}$  and soil organic matter content is not applicable. Clay content, nature of the clay minerals and cation exchange capacity of the soils (Table 1) may be expected to give better predictions of the adsorption of a compound like pirimicarb.

The adsorption isotherms are not strictly linear; the adsorption at the lower concentrations in solution is comparatively high. The Freundlich adsorption equation (Eq. 2) accounts for such deviation from linearity. The Freundlich plots of the adsorption measurements are given in Figure 1. The plots are suitable to represent adsorption data for such a wide range of concentrations in solution. The adsorption at intermediate concentrations was somewhat lower than expected from the Freundlich equation. The values of the Freundlich adsorption coefficient,  $K_f$ , and of the corresponding exponent are given in Table 3. The Freundlich exponents lower than 1.0 indicate that the adsorption isotherm shows a clear curvature. At low concentrations the slope of the adsorption isotherm is steeper than at the higher concentrations.



**Fig. 1** Freundlich plot for the adsorption of pirimicarb onto the soils of Numansdorp and Zeewolde

### 3.2 Rate of transformation in the soils

The results for the incubation of pirimicarb in the two soils are given in Table 4. The amounts remaining at various times were expressed as the fraction of the amount measured at time zero. The initial amount of pirimicarb extracted from the Numansdorp soil was 98% of the amount added; for the Zeewolde soil it was 83% of the amount added. At the end of the incubation period (after 49 days) about half of the dosage of pirimicarb was left in the soil.

The transformation of pirimicarb in the Numansdorp soil (Table 4) can be approximately described with the first-order rate equation (Eq. 4), with rate coefficient  $k_T = 0.0125 \text{ d}^{-1}$ . The corresponding half-life is 55 days. The rate of decline in the first few days of the incubation was comparatively high.

The transformation of pirimicarb in the Zeewolde soil (Table 4) can also be approximately described with the first-order rate equation, now with rate coefficient  $k_T = 0.0136 \text{ d}^{-1}$ . This corresponds to a half-life of 51 days. In this soil too, the rate of decline in the first few days of the incubation was comparatively high.

**Table 4** Fractions of the dosage of pirimicarb remaining with time in the incubation study at 15 °C with the soils from Numansdorp and Zeewolde. The amount measured at time zero was set at 1.00

Incubation time (days)	Fraction remaining in soil from			
	Numansdorp		Zeewolde	
	Series A	Series B	Series A	Series B
0	1.00	1.00	1.00	1.00
1	0.81	0.77	0.90	0.83
2	0.82	0.78	0.75	0.77
3	0.56	0.76	0.79	0.76
7	0.50	0.75	0.73	0.71
14	0.46	0.71	0.71	0.75
21	0.45	0.64	0.65	0.65
30	0.43	0.58	0.56	0.60
35	0.42	0.59	0.52	0.59
42	0.39	0.58	0.45	0.51
49	0.39	0.50	0.49	0.40

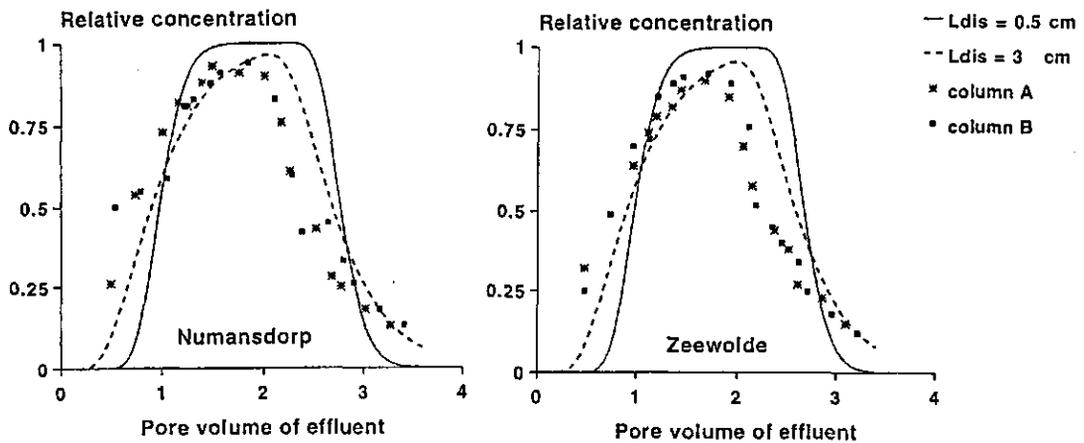
### 3.3 Leaching in the soil columns

#### 3.3.1 The tracer bromide-ion

The results of the leaching experiment with bromide-ion in the Numansdorp soil columns are given in Figure 2. The tracer appears rather quickly at high concentrations in the effluent. At pore volumes of effluent around 2.0, the concentrations are at the maximum level and they approach the feed concentration of bromide-ion. The decline of the concentration after the maximum level is also rapid, but the effluent curve shows distinct tailing later on. The leaching pattern was roughly the same for the two Numansdorp soil columns.

The results of the simulation of the leaching of bromide-ion in the Numansdorp soil are also given in Figure 2. The simulation with a dispersion distance  $L_{dis} = 0.5$  cm resulted in the sides of the effluent curve being too steep. The simulation with  $L_{dis} = 3.0$  cm resulted in a rather good description of the spreading in the effluent curve. However, the measured breakthrough of bromide-ion was earlier than that computed. Also, the measured depletion of bromide-ion from the columns was faster than computed, except for the tailing part of the distribution.

The results of the leaching experiment with bromide-ion in the Zeewolde columns are also given in Figure 2. Again, the measured effluent curve is compared with that computed with the simulation model. The higher dispersion distance  $L_{dis} = 3.0$  cm gives a much better description of the spreading in the curve than  $L_{dis} = 0.5$  cm. The maximum concentration level around two pore volumes of effluent remained somewhat lower than the feed concentration. At 0.5 pore volume of effluent, bromide-ion



**Fig. 2** Leaching of the tracer bromide-ion from the Numansdorp soil columns A and B and the Zeewolde soil Columns A and B. Effluent concentrations relative to the feed concentration. Signs: measured values. Lines: effluent curves computed with dispersion distance 0.5 cm and 3.0 cm

appeared at higher concentrations in the effluent than was simulated with the computation model. Corresponding to this, the decline of the effluent concentration from the maximum level started earlier than computed. However, the measured effluent concentrations show distinct tailing.

The comparatively high concentrations of bromide-ion in the early effluent fractions from the soil columns indicate that a fraction of the water phase flowed at a comparatively high rate. This fraction flowed at a rate higher than that corresponding to uniform water flow through the columns. The fast decline of the concentrations at the back-hand side of the effluent curves also point to a quickly flowing fraction of the water phase. On the other hand, the tailing in the effluent curves indicates that another part of the water phase flowed comparatively slowly. Presumably, the bromide-ions that diffused into the more stagnant regions of the water phase had to diffuse back into the regions with higher flow rate before substantial convective transport could occur.

### 3.3.2 Pirimicarb

The distribution of pirimicarb in the soil columns Numansdorp A and Zeewolde A, measured at the end of the leaching period, is given in Table 5. The highest concentrations were still present in the top of the soil columns. Below 0.1 m depth there was a rather level distribution with depth to the bottom end of the columns. The movement in the Zeewolde column was somewhat less than that in the Numansdorp column. This corresponds to the stronger adsorption of pirimicarb in the Zeewolde soil (Table 3). The results for the duplicate columns B are not given because the separation of the peaks in the chromatograms was inadequate.

An estimate can be made of the mass of pirimicarb remaining in the soil columns at the end of the leaching period. Because only a fraction of the soil layers was analysed (Table 5), the missing concentrations had to be estimated by interpolation. The mass of pirimicarb remaining in the Numansdorp A column was estimated to be 48% of the dosage, while the mass remaining in the Zeewolde A column was estimated to be 46%.

*Table 5 Concentration of pirimicarb at different depths in the soil columns Numansdorp A and Zeewolde A at the end of the leaching period*

Numansdorp A		Zeewolde A	
Layer (m)	Concentration ( $\mu\text{g}/\text{cm}^3$ )	Layer (m)	Concentration ( $\mu\text{g}/\text{cm}^3$ )
0 -0.03	0.39	0 -0.02	0.73
0.05-0.07	0.30	0.04-0.06	0.19
0.11-0.13	0.07	0.10-0.12	0.10
0.15-0.17	0.10	0.14-0.16	0.07
0.19-0.21	0.06	0.18-0.20	0.02
0.23-0.25	0.07	0.22-0.24	0.02

The concentrations of pirimicarb in the effluent of the soil columns from Numansdorp at different sampling days are given in Table 6. The insecticide appeared already in the first effluent fractions, be it at a very low level. After that, the concentration increased somewhat but it tended to level-off in the second half of the leaching period.

The concentrations of pirimicarb in the effluent of the soil columns from Zeewolde are given in Table 7. The insecticide came out very soon at a low level. For Column A the concentration increased somewhat with time, but for Column B it remained at the low initial level.

The effluent curves indicate that there was a comparatively fast leaching of a small fraction of the pirimicarb distribution in the soil columns. This means that a small fraction of the water phase was very mobile. The extent of adsorption of pirimicarb in the soil columns seemed to increase with time. This caused the effluent concentrations to level-off, while the peak of the distribution was still in the soil columns.

The total mass of pirimicarb leached from the soil columns can be calculated from the concentrations and the volumes of the corresponding effluent fractions. Because not all the effluent fractions were analysed, the missing concentrations had to be estimated by interpolation. The total masses of pirimicarb leached from the Numansdorp soil columns were estimated to be at most 62  $\mu\text{g}$  (Column A) and 68  $\mu\text{g}$  (Column B), respectively. This corresponds to at most 6.2 % and 6.8% of the dosage, respectively. As there was possibly a small contribution of interfering substances to the detector response, the actual percentages leached may have been somewhat lower.

**Table 6** Concentrations of pirimicarb measured in the effluent of the Numansdorp soil columns

Sampling day	Column A		Column B	
	Volume of effluent (mL)	Concentration (ng/mL)	Volume of effluent (mL)	Concentration (ng/mL)
1	251	6.1	255	6.6
3	242	3.8	254	9.0
5	246	3.3	250	12.6
8	246	6.1	252	10.1
10	259	9.0	250	11.4
12	248	9.6	-	-
13	-	-	257	12.2
14	252	13.0	-	-
16	250	14.2	252	11.0
19	246	16.3	247	12.2
21	238	15.4	-	-
22	273	16.3	256	10.9
24	249	15.2	266	11.8

**Table 7** Concentrations of pirimicarb measured in the effluent of the Zeewolde soil columns

Sampling day	Column A		Column B	
	Volume of effluent (mL)	Concentration (ng/mL)	Volume of effluent (mL)	Concentration (ng/mL)
1	251	3.8	251	3.4
3	244	6.5	248	3.7
5	258	10.3	259	3.1
8	248	7.6	251	2.9
10	252	9.0	251	2.8
12	-	-	252	3.3
13	247	9.8	-	-
14	-	-	247	4.4
16	246	8.6	250	3.4
19	248	9.6	-	-
21	-	-	244	1.7
22	251	8.4	254	1.6
24	260	9.4	236	2.7

The total masses of pirimicarb leached from the Zeewolde soil columns were at most 51  $\mu\text{g}$  (Column A) and 18  $\mu\text{g}$  (Column B), respectively. This corresponds to at most 5.1% and 1.8% of the mass of pirimicarb applied to the columns. Again, the actual percentages leached may have been somewhat lower, due to a small contribution of interfering substances. Presumably, the lower percentages leached from the Zeewolde soil, as compared to the Numansdorp soil, are related to the stronger adsorption of pirimicarb in the Zeewolde soil (Table 3).

The average movement of pirimicarb (= position of the peak of the distribution) in the Numansdorp and Zeewolde soil columns was estimated using Eq. 5. The average distance of movement in the Numansdorp soil was estimated to be  $z_a = 0.30$  m. For the Zeewolde soil columns,  $z_a$  was estimated to be 0.18 m. So one would expect that the top of the distribution of pirimicarb had leached from the soil columns or had leached to the lower part of the soil columns, respectively. It is clear that the movement of the major part of the distribution of pirimicarb is much more slowly than expected on the basis of the adsorption coefficients.

With a daily irrigation (and thus outflow) of 0.0225 m/day, pirimicarb would be expected to move on average 0.012 and 0.008 m per day, respectively, in the Numansdorp and Zeewolde soils. This means that a small fraction of the insecticide moved at a much higher rate than expected from the combination of uniform water flow and the measured adsorption coefficients.

The estimations show that a computation model simulating uniform water flow and instantaneous adsorption/desorption equilibration is not suitable for describing the movement of a pesticide like pirimicarb in structured loamy soils with a rather high flow rate of water.

#### 4 GENERAL DISCUSSION AND CONCLUSIONS

The adsorption coefficients  $K_d$  of 1.3 and 2.4 dm<sup>3</sup>/kg measured in the present study point to moderate adsorption of pirimicarb onto the loamy fruit orchard soils. The adsorption coefficient  $K_d$  measured by Sanchez-Camazano & Sanchez-Martin (1988) for 21 Spanish soils ranged from about 0.5 to 6.5 dm<sup>3</sup>/kg, with an average value of 2.5 dm<sup>3</sup>/kg. The range measured for the Spanish soils is very wide. The adsorption coefficients measured in the present study allow a more narrow range in the first estimates of the leaching of pirimicarb from soils.

Approximation of the present adsorption data with the Freundlich isotherm yields values of the Freundlich exponent distinctly below 1.0. This means that there is a substantial curvature in the adsorption isotherm. Such a curvature shows up most clearly if the range of concentrations is very wide, as in the present study. If such a curvature in the isotherm is introduced into the computer-simulations, a distinctly lower leaching is computed than with the approximate linear adsorption isotherm with slope  $K_d$ . The Freundlich equation accounts for comparatively strong adsorption (steeper isotherm) at the lower pesticide concentrations in soil.

In the incubation period of 49 days at 15 °C, pirimicarb was transformed in the soils to about half of its initial amount. The approximate first-order rate coefficient was  $k_T = 0.0125 \text{ d}^{-1}$  (half-life 55 days) for the Numansdorp soil. The corresponding rate coefficient for the Zeewolde soil was  $0.0136 \text{ d}^{-1}$  (half-life = 51 days). For estimating the extent of leaching in the field, the rate coefficients and half-lives have to be translated to the reference temperature of 20 °C (Boesten & van der Linden, 1991). The resulting half-life at 20 °C is 37 days for the Numansdorp soil and it is 34 days for the Zeewolde soil.

On the basis of the adsorption coefficients and the transformation rate coefficients measured in the present study, first estimates can be made of the leaching of pirimicarb from loamy orchard soils to the upper groundwater. Brouwer (1989) presented results of computations with the PESTLA model on the leaching after application of hypothetical pesticides to a loamy soil in spring. Because a direct use of  $K_{om}$  values is not justified for a compound like pirimicarb, an equivalent  $K_{om,eq}$  is calculated from the  $K_d$ -value measured in the present study and the  $K_d$  value for the hypothetical pesticides in the computations of Brouwer (1989). The value calculated for the Numansdorp soil is  $K_{om,eq} = 39 \text{ dm}^3/\text{kg}$ . This value should be combined with the half-life of 37 days estimated for the reference temperature (20 °C). For the dosage of pirimicarb in current fruit growing of 0.6 kg/ha, the estimated leaching concentration is 0.01 µg/L. For the reduced dosage of 0.34 kg/ha in the integrated fruit growing experiment, this estimated concentration is half of this.

The calculated value of  $K_{om,eq}$  for the Zeewolde soil is 72 dm<sup>3</sup>/kg. This value should be combined with the half-life of 34 days estimated for the reference temperature (20 °C). For the dosage of pirimicarb in current fruit production of 0.6 kg/ha, the estimated leaching concentration is less than 0.001 µg/L. For the reduced dosage of

0.34 kg/ha in the integrated fruit production experiment, the estimated concentration is even lower. The difference in estimated leaching concentration for the two soils is caused by the combination of stronger adsorption and faster transformation in the Zeewolde soil.

In the estimations above, it is assumed that the full dosage of pirimicarb penetrates into the soil. However, the application is directed to the crop, so only a fraction of the dosage will deposit on the soil surface. Further, processes like volatilization and photochemical transformation may be expected to accelerate the decline of pirimicarb at the plant and soil surfaces (Leistra, 1992). Presumably, only a small fraction of the pirimicarb dosage penetrates into the soil, so a second estimate of the leaching concentration will lead to even lower values.

Bromide-ion was used in the leaching experiment as a tracer for water flow in the soil columns. A fraction of the water phase was found to flow much faster than expected from uniform water flow. On the other hand, the tailing in the effluent curve showed that a fraction of the bromide-ion had diffused into more stagnant regions of the soil water phase. The tailing shows that it took some time for this fraction to diffuse back to the more mobile part of the water phase.

After the total irrigation corresponding to 0.54 m water layer had been applied to the soil columns in 24 days, most of the pirimicarb distribution was still present in the top of the soil columns. In the lower part of the soil columns, the distribution was rather level down to the bottom end of the columns. The movement of the main part of the distribution was much less than expected on the basis of the adsorption coefficients. On the other hand, a small fraction of the pesticide distribution appeared very soon in the effluent. The amount of pirimicarb leaching from the columns of Numansdorp and Zeewolde soil was estimated to be about 6.5% and 3.5% of the dosage, respectively.

The estimations show that a computation model simulating uniform water flow and instantaneous adsorption/desorption equilibration is not suitable for describing the movement of a pesticide like pirimicarb in structured loamy soils at a rather high flow rate of water.

At high rates of water supply to structured loamy soils, like in the present column study, a fraction of the soil water phase flows comparatively fast, presumably through the larger voids. This water takes some of the pesticide with it, especially in the first period after application. Gradually, the pesticide moves into the smaller soil pores, with mainly stagnant soil water. Bromide-ion is hardly adsorbed by soils; it is even repelled by the negatively charged surfaces (e.g. of the clay minerals). So the ion can diffuse gradually back to the moving regions of the water phase. However, the weak base pirimicarb is distinctly adsorbed, e.g. by the negatively-charged surfaces of the clay minerals, upon penetration into the smaller pores. In the course of time, the extent of adsorption may be expected to increase. Therefore, the release of pirimicarb from the adsorbing surfaces in the stagnant region of the soil water phase can be expected to be much more slowly than that of bromide-ion.

With respect to the risk of leaching of pirimicarb from loamy soils in the field, the residence time of the insecticide in the soil may be expected to have a great effect. Older residues may be less available for transport with the mobile regions of the water phase than more recent residues, because they are largely adsorbed on the surfaces in the smaller pores with stagnant water phase.

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