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# Movement of water, bromide and the pesticides ethoprophos and bentazone in a sandy soil: the Vredepeel data set

J.J.T.I. Boesten<sup>\*</sup>, L.J.T. van der Pas

*Alterra Green World Research, Wageningen University and Research Centre,  
PO Box 47, 6700 AA Wageningen, The Netherlands*

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## Abstract

The aim of this study was to collect a data set suitable for testing pesticide leaching models in the case of a Dutch sandy soil with a shallow groundwater table. The movement of water, bromide ion and the behaviour of the pesticides ethoprophos and bentazone was studied. The substances were applied after sowing winter wheat in autumn 1990. This late application time is unusual for bentazone: it was selected on scientific grounds (without agricultural purpose). Rainfall, groundwater level and soil temperature were monitored continuously at the experimental field (80 m long and 54 m wide) until spring 1992. Soil profiles were sampled at 1, 103, 278 and 474 days after application (16 profiles at each date). In the laboratory, pesticide transformation rates were measured with soil material from 0–25, 50–100 and 100–200 cm depth. Sorption isotherms were measured with material from 0–25 cm depth. Concentration profiles showed that mobility increased in the sequence ethoprophos — bentazone — bromide ion. Ethoprophos movement was limited to the top 25 cm layer whereas bentazone leached to below 1 m depth. At the end of the study, the concentrations of ethoprophos and bentazone were below the detection limit ( $0.2\text{--}2\ \mu\text{g dm}^{-3}$ ) in all soil layers between 25 and 120 cm depth. Recommended values for the most important input parameters of pesticide leaching models are presented. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Field experiment; Soil; Modelling; Pesticides; Bromide ion; Ethoprophos; Bentazone

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## 1. Introduction

Leaching of pesticides to groundwater is an important environmental aspect of the pesticide use in agriculture. In the Dutch registration procedure, a first assessment of

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<sup>\*</sup> Corresponding author. Tel.: +31-317-474343; fax: +31-317-424812.

*E-mail address:* boesten@alterra.wag-ur.nl (J.J.T.I. Boesten).

pesticide leaching is based on calculations with the PESTLA model for a standard scenario described by van der Linden and Boesten (1989); Boesten and van der Linden (1991). This scenario consists of a sandy soil with (i) a low organic matter content below the plough layer, (ii) a shallow groundwater table and (iii) continuous maize cropping. It was selected because it is representative for soils near water pumping stations in the eastern part of the Netherlands. However, PESTLA had not been tested so far at a field scale for a situation similar to that assumed in the scenario. Therefore, a field experiment was set up in 1990 to obtain an appropriate data set. Also flow of water and movement of bromide ion were included in the experiment because this enables testing or calibration of the sub-models for water flow and solute movement which is essential for a meaningful test of simulation models (Vanclooster et al., 2000). Two pesticides were selected: bentazone which is mobile (Abernathy and Wax, 1973) and ethoprophos which is moderately sorbed and has a low mobility (Leistra and Smelt, 1981). The data set is described in full detail by Boesten and van der Pas (1999) and was made available to all interested modellers within the COST66 action in 1996.

## 2. Procedures for the field experiment

### 2.1. *Experimental field and soil profile*

The experimental field was located at the experimental farm 'Vredepeel' in the municipality Vredepeel in the province Limburg in the southeastern part of the Netherlands (North latitude  $51^{\circ}32'$ , East longitude  $5^{\circ}52'$ , altitude 27 m a.s.l.). The soil was a gley podzol (FAO classification). There was no sub-surface drainage. The experimental field was 80 m long and 54 m wide (the 80 m length was approximately in the north–south direction). It was divided into 16 plots each 10 m long and 27 m wide. Each plot was subdivided into 27 sub-plots (3.3 m long and 3.0 m wide) of which 17 sub-plots per plot could be sampled (sub-plots that were intersected by wheel tracks were excluded). A sub-plot could only be sampled once because of disturbance of the crop and soil surface around the sampling site. The field was practically flat in the north–south direction. In the east–west direction there was a small slope: the soil levels of the eastern and western parts of the field were practically flat but the western part was about 20 cm lower than the eastern part.

Soil properties were measured using the soil samples collected for the laboratory studies with the pesticides (see below for sampling procedure). The results in Table 1 show a sharp gradient in the organic carbon profile (2.3% in the 0–25 cm layer and 0.1% below 50 cm depth). This gradient could easily be observed in the field by the gradient in the colour of the soil: the sequence is black — brown — yellow — grey with increasing depth. The depths of transitions between the layers were measured at 31 spots. The average depth of transition between black and brown was 32 cm and the standard deviation of this average was 0.6 cm (range 27–40 cm). The average depth of transition between brown and yellow was 49 cm with a standard deviation of 1.7 cm (range 35–70 cm). The soil characteristics listed in Table 1 were not measured for the brown layer.

In 1990, sugar beets were grown at the experimental field: the beets were harvested in October 1990 but the leaves were incorporated into the soil. On 22 November 1990

Table 1

Characteristics of the Vredepeel soil samples used for the laboratory measurements on pesticide sorption and transformation. Figures between parentheses indicate standard deviations of three individual measurements

Property	Soil layer		
	0–25 cm	50–100 cm	100–200 cm
pH-KCl	5.3	4.7	4.6
Mass fraction of			
Organic matter (%)	4.9 (0.0)		
Organic carbon (%)	2.29 (0.03)	0.11 (0.02)	0.12 (0.06)
CaCO <sub>3</sub> (%)	0.1		
Clay (0–2 mm in %)	3	2	3
Silt (2–50 mm in %)	6	2	9
Sand (50–2000 mm in %)	91	96	88

winter wheat was sown at a depth of 3–5 cm and at a row distance of 15 cm with a machine that combined soil cultivation and sowing. All chemicals were sprayed a few hours after sowing the winter wheat. Usually, bentazone is applied in spring or summer but in this study it was applied in November solely for scientific reasons (without agricultural purpose). In March 1991, a nitrogen fertiliser was applied. The winter wheat was harvested at 14 August 1991. On 28 August 1991 pig slurry (dry-matter content of 6%) was applied at a rate of 28 m<sup>3</sup> ha<sup>-1</sup>. The slurry was incorporated in the top 15 cm at the same day. In September 1991 yellow mustard was sown as green manure. On 29 November 1991 the mustard was incorporated into the top 15–20 cm of the soil by rotary cultivation. The field experiment was stopped on 10 March 1992.

According to the records of the experimental farm, ethoprophos had never been applied to the experimental field.

## 2.2. Application of the chemicals

All chemicals were applied between 15 and 17 h on 22 November 1990 with a common field sprayer (18 m long) provided with ceramic Teejet nozzles (Type 11004). The experimental field was sprayed twice. The first time bentazone and ethoprophos were mixed in the tank and sprayed (using an areic volume of water of 430 l ha<sup>-1</sup>). The second time KBr was sprayed (also at 430 l ha<sup>-1</sup>). The formulated products used were the wetttable powder Basagran and the liquid formulation MOCAP<sup>R</sup>20. The calculated doses of bentazone, ethoprophos and bromide were 0.80, 3.35 and 111 kg ha<sup>-1</sup>, respectively. The temperature during spraying was about 8°C and no rain fell. There was practically no wind.

## 2.3. Monitoring of meteorological data, groundwater level and soil temperature

Rainfall was recorded with two rain gauges. The first was a Lambrecht rain gauge installed at 400 m distance of the experimental field. Its aperture was 1.2 m above the soil

surface. This gauge measured rainfall continuously with a pen and recording paper. The second gauge was a Hellmann rain gauge installed at the border of the experimental field with its rim flush with the soil surface. With this gauge cumulative rainfall over periods of 1–3 weeks was measured. The measurements with the Hellmann gauge were made because measurements made flush with the soil surface are more accurate than measurements made at 1.2 m height: in general the amount of rainfall recorded decreases with increasing height of aperture (Beese and van der Ploeg, 1978). Over the whole experimental period the Hellmann gauge recorded indeed 16% more rain than the Lambrecht gauge. Daily rainfall derived from the Lambrecht gauge was multiplied with the Hellmann/Lambrecht quotient of the cumulative rain for the corresponding period.

At 400 m distance of the experimental field, daily minimum and maximum air temperature were measured. Meteorological data on daily global radiation, average wind speed and air humidity were derived from meteorological stations at 25–65 km distance.

Groundwater level was continuously measured at two spots at the border of the experimental field. Differences between daily values of the two spots were only a few centimetres and they were averaged. Soil temperature at 2.5 cm depth was measured continuously at the experimental field.

#### *2.4. Sampling of soil profiles*

Soil profiles were sampled at seven times (at 1, 22, 42, 103, 214, 278 and 474 days after application). The first sampling was started in the morning of 23 November, less than 1 day after spraying. No rain fell between spraying and this first sampling. At each sampling time, 16 soil profiles were sampled (one from each plot and taken from a subplot that was randomly selected). The top 30 cm of soil was sampled with a split-tube auger with a cutting ring of inner diameter 95 mm. The soil core was sliced into four sections 7.5 cm thick (the top layer was subdivided in two sections of 4.0 and 3.5 cm). The 30–120 cm soil layer was sampled with a motor-driven soil core sampler (split tube with inner diameter of 10 cm) as described by Hendrickx et al. (1991). The split tube with the sample was opened and the outer few millimetres of soil were scraped from the soil column to remove any contamination with soil from a shallower layer (by driving the tube into the soil, soil particles may move downwards along the wall of the tube). Below 30 cm depth two types of sample were taken from marked 7.5 cm thick layers: samples taken with a steel ring for determination of bulk density, volume fraction of liquid and bromide concentration and samples taken by a scoop for determination of pesticide concentrations. The steel rings (volume 100 cm<sup>3</sup>) were pushed in the centre of the marked 7.5 cm layers. The remaining soil around the ring was carefully collected with a scoop and put into a plastic bag. The soil samples taken for pesticide analysis were combined for the layers 30–45, 45–60, 60–90 and 90–120 cm. Because pesticide analysis is laborious, the soil samples from all spots were not analysed individually. The experimental field was divided into four sectors which consisted of four plots each. Equal masses of moist soil from the layers sampled between the same depths and from the four plots in one sector were combined and mixed before extraction.

## 2.5. Analyses of soil profiles

Bulk density and volume fraction of liquid were determined by drying soil samples for 3 days at 70°C. Bromide ion was extracted by shaking soil samples with demineralised water at solid–liquid ratio of about 1 kg dm<sup>-3</sup>. The bromide concentration in the extracts was measured with high pressure liquid chromatography using spectrophotometric detection. Ethoprophos was extracted by shaking 100 g of moist soil with 50 cm<sup>3</sup> CaCl<sub>2</sub> solution (0.01 mol dm<sup>-3</sup>) and 50 cm<sup>3</sup> hexane for 1 h. The ethoprophos concentration in the hexane extracts was measured with gas liquid chromatography using a nitrogen–phosphorus or a flame photometric detector. The extraction efficiency was 87–93%. The detection limit for soil was 0.2–0.5 µg dm<sup>-3</sup>. Bentazone was extracted by shaking 100 g of moist soil with 50 cm<sup>3</sup> of a mixture of acetone and water (50/50 by volume) for 1 h. The supernatant was collected and acidified with 0.5 cm<sup>3</sup> concentrated HCl. Dichloromethane (25 cm<sup>3</sup>) was added and the mixture was shaken for 1 h. The bentazone concentration in the dichloromethane extracts was measured with high pressure liquid chromatography using spectrophotometric detection. The extraction efficiency was 86–96%. The detection limit for soil was 1–3 µg dm<sup>-3</sup>. The measured concentrations of bromide, ethoprophos and bentazone were not corrected for the extraction efficiency.

## 3. Procedures for laboratory experiments

### 3.1. Soil hydraulic properties

Water retention and conductivity characteristics were measured for soil samples taken from only one pit at the experimental field using procedures as described by Boels et al. (1978); Stolte et al. (1992). Soil samples were taken from three depths: 10–18 cm (a sample from the black layer), 45–53 cm layer (sample from the brown layer) and 65–78 cm depth (sample from the yellow layer). The volume of the soil samples ranged between 300 and 600 cm<sup>3</sup>.

### 3.2. Incubation studies with pesticides

#### 3.2.1. Soil sampling and soil treatment

The transformation rate of both pesticides was measured in samples from the 0–25, 50–100 and 100–200 cm layers. The sample from the 0–25 cm layer was taken in October 1990 before harvest of the sugar beets. It was taken using an auger from 70 spots distributed regularly over the experimental field. The soil samples from the 50–100 and 100–200 cm layers were taken from 16 holes (one in each plot) around 8 November 1990. At the sampling time the groundwater level was at 120 cm depth so the 100–200 cm sample was taken from a water-saturated soil layer. The samples taken from the 100–200 cm layer were, therefore, collected in a vessel to which sufficient groundwater was added in the field to fill it completely. The soil sample from the 0–25 cm layer was stored in the laboratory at 5°C and the 50–100 and 100–200 cm samples were stored at 10°C.

Time between collection of samples in the field and the start of the corresponding incubation study was about 1 month.

### 3.2.2. *Incubation in soil from the 0–25 cm layer*

Ethoprophos was incubated at 5, 15 and 25°C and bentazone at 5 and 15°C. Portions of 50 g of moist soil were added to glass jars. A volume of 2 cm<sup>3</sup> of distilled water containing either ethoprophos or bentazone was added to each jar and mixed through the soil (so a jar contained either ethoprophos or bentazone). The jars were closed with aluminium foil in which a hole (3 mm) was made to ensure aerobic conditions in the head space of the system. Moisture content during incubation was 0.15 kg kg<sup>-1</sup>. The dose of ethoprophos corresponded with an initial content of 5.7 mg kg<sup>-1</sup> and the dose of bentazone corresponded with 1.2 mg kg<sup>-1</sup>. Half of the incubated jars were used to follow the transformation by extraction with organic solvent. The other half were used to measure the concentration in liquid phase to assess effects of long-term sorption kinetics. The first half of the jars were treated as follows. The soil in the jars containing ethoprophos was extracted by adding 25 cm<sup>3</sup> of water containing CaCl<sub>2</sub> (0.01 mol dm<sup>-3</sup>) and 25 or 50 cm<sup>3</sup> of hexane. The soil in the jars containing bentazone was extracted by adding 50 cm<sup>3</sup> of a mixture of acetone and water (50/50 by volume). The further procedures for the extractions and the chemical analyses were identical to those used for the samples from the soil profile. The second half of the jars were treated as follows. The liquid phase of the moist soil was collected with a centrifuge tube (Boesten, 1986). After centrifugation, 0.5–2.5 cm<sup>3</sup> of water was collected in the lower compartment. The concentration of bentazone was measured by direct analysis in the water and that of ethoprophos after extraction with hexane. The procedures for the chemical analyses were the same as before. Concentrations of ethoprophos in the liquid phase were corrected for sorption to glass filters by dividing them by 0.83 (as was derived from a separate experiment).

### 3.2.3. *Incubation in soil from the 50–100 and 100–200 cm layers*

The transformation rates in the 50–100 and 100–200 cm layers were measured at 10°C. Portions of 100 g of moist soil from the 50–100 cm layer were weighed into glass. Moisture content during incubation was 0.11 kg kg<sup>-1</sup>. The pesticides were added to a jar in 1 cm<sup>3</sup> of distilled water that contained ethoprophos or bentazone. The content of ethoprophos was about 12 µg kg<sup>-1</sup> at the start and that of bentazone was about 120 µg kg<sup>-1</sup>. Portions of the material from the 100–200 cm layer were transferred to glass jars (volume 0.5 dm<sup>3</sup>) with a small cylinder as described by Boesten et al. (1991). The mass of dry soil added to the jars was on average 93 g and the mass of water added was on average 25 g. This implied that the soil in the jars was water-saturated with a water layer of a few millimetres thickness on top. The pesticides were added in the same way as for the 50–100 cm layer. The initial contents (on a dry soil basis) of both pesticides were about equal to those for the 50–100 cm layer. Both the glass jars containing the 50–100 cm material and those containing the 100–200 cm material were covered with aluminium foil in which a hole with a diameter of 3 mm was made to ensure aerobic conditions in the head space. The jars containing ethoprophos were extracted by adding 25 cm<sup>3</sup> of aqueous CaCl<sub>2</sub> solution (0.01 mol dm<sup>-3</sup>) plus 50 cm<sup>3</sup> hexane. The jars

with bentazone were extracted by adding 50 cm<sup>3</sup> of a mixture of acetone and water (50/50 by volume). The further procedures and analyses were identical to those for the samples from the soil profile.

### 3.3. *Measurement of sorption of the pesticides in soil–water suspensions*

Soil–water suspension measurements were made with soil material from the 0–25 cm layer. The sorption of ethoprophos was determined at 5 and 25°C and that of bentazone at 5 and 15°C. The soil sample was from the same batch as used for the incubation studies. It had been stored in the laboratory for 13–15 months at 5°C. The moisture content was 0.10 kg kg<sup>-1</sup>. Solutions of ethoprophos with concentrations of 0.5, 5 and 50 mg dm<sup>-3</sup> were made in distilled water containing 0.01 mol dm<sup>-3</sup> CaCl<sub>2</sub>. A mass of 50 g of moist soil was added to centrifuge tubes with a volume of 90 cm<sup>3</sup>. Then 50 cm<sup>3</sup> of an aqueous ethoprophos solution was added. The centrifuge tubes were rotated at a frequency of 0.3 s<sup>-1</sup> for 24 h and centrifuged at the corresponding temperature. A sample of the water layer (about 25 cm<sup>3</sup>) was collected and extracted with 25 cm<sup>3</sup> hexane by shaking for 1 h. For each temperature and each ethoprophos concentration, three centrifuge tubes were used. The concentration of ethoprophos in the hexane was determined as described before. It was assumed that the decrease of the concentration in the liquid phase was completely attributable to sorption. The procedure for bentazone was identical to that for ethoprophos with the following exceptions: (i) initial concentrations were 0.1, 0.5, 2 and 10 mg dm<sup>-3</sup>, (ii) 25 cm<sup>3</sup> of aqueous bentazone solution was added, (iii) bentazone was not extracted from the aqueous solution; instead the concentrations in the aqueous solutions were directly measured via HPLC as described before. The solid/liquid ratio was set to about 2 g cm<sup>-3</sup> for bentazone to increase the accuracy of the measurement (Boesten, 1990) because low sorption of bentazone was anticipated.

## 4. Results of the field study

The results of the field study (and also of the laboratory study) are available in numerical form on a diskette as part of the report by Boesten and van der Pas (1999). Main results will be presented here graphically. As shown in Fig. 1, air temperature ranged from –15 to 35°C and the daily average temperature at 2.5 cm depth in soil was usually within the range of the daily maximum and minimum air temperatures. Fig. 2 shows that the groundwater level varied from about 50 to 170 cm depth. The daily rainfall data shown in Fig. 2 correspond with 268 mm of cumulative rainfall after 200 days and with 768 mm at the end (after 474 days). Combination of the data on rainfall and groundwater level in Fig. 2 indicates that periods with intensive rainfall in winter (e.g., after about 40 days and just before 400 days) resulted in sharp increases of the groundwater level whereas the rainfall in summer (e.g., after 220 days) hardly influenced the groundwater level. Obviously, the water from the rainfall in summer did not reach the groundwater table in that period. van de Veen and Boesten (1996) showed via simulations with SWACROP (using weather data from a 30-year period) that groundwater level fluctuations as shown in Fig. 2 are quite common for such a soil under Dutch conditions.

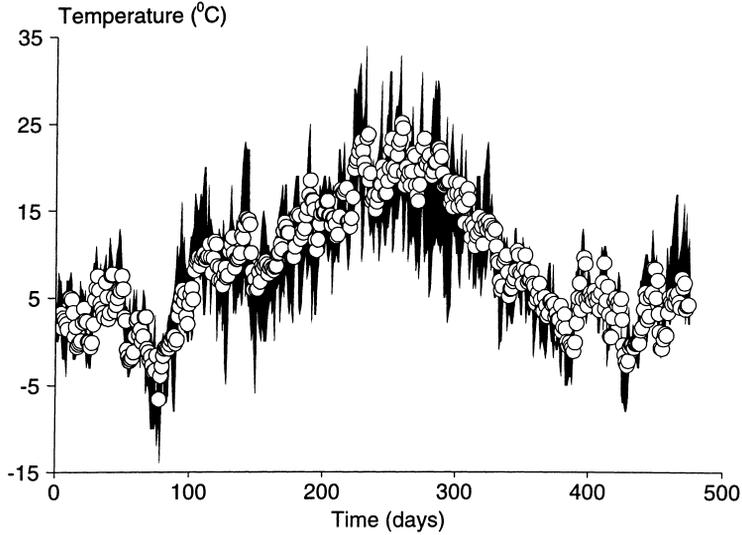


Fig. 1. Daily average soil temperature at 2.5 cm depth and daily minimum and maximum air temperatures measured at the experimental field. Time zero corresponds with 0.00 hours at 23 November 1990. The points are soil temperatures and the area is the range of the air temperature.

The bulk density increased almost continuously with increasing depth from about  $1.3 \text{ kg dm}^{-3}$  at the soil surface to about  $1.7 \text{ kg dm}^{-3}$  at 1.2 m depth. Moisture and concentration profiles are presented as sampled immediately after application (1 day), at the end of the first winter (103 days), after harvest of the winter wheat in August

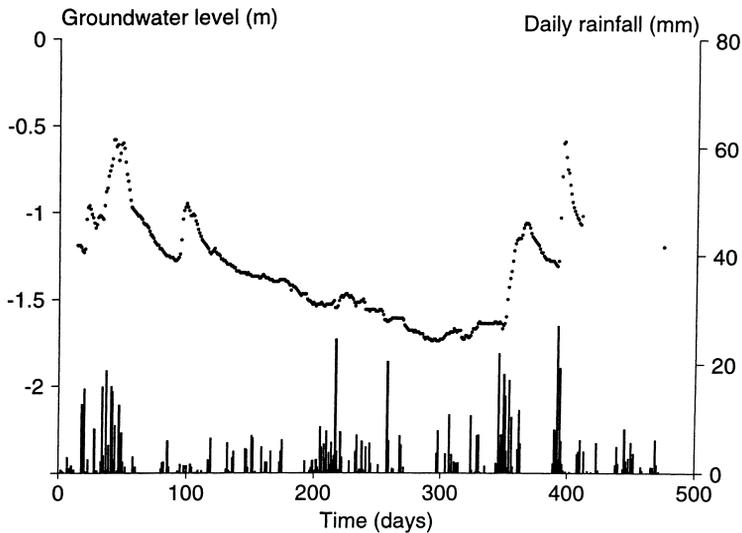


Fig. 2. Daily average groundwater level and daily rainfall measured at the experimental field. Time zero corresponds with 0.00 hours at 23 November 1990. Points are groundwater levels and bars are rainfall.

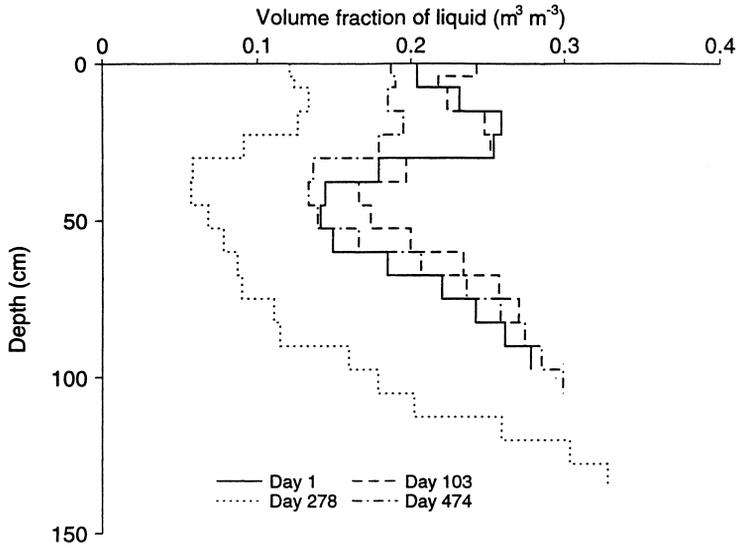


Fig. 3. Average volume fraction of liquid as a function of depth as measured at the experimental field at 1, 103, 278 and 474 days after application.

(278 days) and at the end of the experiment in the second winter (474 days). The measured moisture profiles (Fig. 3) show that the profiles measured in autumn and winter (1, 103 and 474 days) were similar and much wetter than the profile after harvest of the wheat (278 days). Fig. 3 shows also that the volume fraction of liquid in the top 30 cm was always higher than that in the 30–60 cm layer. This is probably caused by the much larger organic matter content of the top 30 cm which leads to a higher water retention capacity. Below 60 cm the volume fraction of liquid increased always with increasing depth probably due to the influence of the groundwater table.

At 1 day after spraying the average recovered areic<sup>1</sup> mass of bromide was  $105 \text{ kg ha}^{-1}$ ; the SD of this average was  $7 \text{ kg ha}^{-1}$ . So the areic mass recovered from soil corresponded well with the areic mass sprayed onto the soil surface ( $111 \text{ kg ha}^{-1}$ ). Almost all bromide was recovered from the 0–4 cm layer whose bromide concentration was  $258 \text{ mg dm}^{-3}$ . In the 4–7.5 cm layer a concentration of  $1.0 \text{ mg dm}^{-3}$  was found (probably an artefact resulting from contamination from the top layer during sampling in the field). At greater depths the average concentration was always below the detection limit of  $0.7 \text{ mg dm}^{-3}$ . The results for the other sampling dates are shown in Fig. 4. After 103 d (at the end of the first winter) the bromide concentration increases with increasing depth. After 278 days the distribution of bromide with depth is very flat. At the end of the study (after 474 days), the distribution is also flat but at a lower concentration level.

At 1 day after spraying the average recovered areic mass of ethoprophos was  $2.7 \text{ kg ha}^{-1}$ ; the SD of this average was  $0.1 \text{ kg ha}^{-1}$ . The measured concentrations were not corrected for recovery which was 89% for the 0–25 cm layer. So correction for

<sup>1</sup> 'Areic' means 'divided by area' (Rigg et al., 1985).

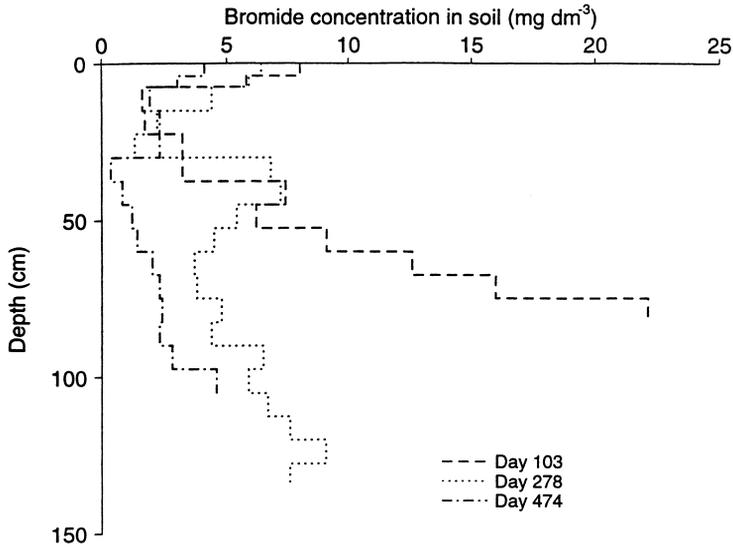


Fig. 4. Average concentration of bromide ion as a function of depth as measured at the experimental field at 103, 278 and 474 days after application.

recovery results in an recovered amount of  $3.0 \text{ kg ha}^{-1}$ . This corresponded reasonably well with the areic mass sprayed onto the soil surface ( $3.35 \text{ kg ha}^{-1}$ ). The highest concentrations of ethoprophos after 1 day were measured in the 0–4 cm layer: the average concentration in the 4–7.5 cm layer was only 0.2% of that in the 0–4 cm layer. Because no rain fell between spraying and sampling this 0.2% must be the result of contamination due to the sampling procedure: transfer of 0.2% to the next layer implies a very limited sampling contamination. Concentrations in the 60–67.5 and 90–97.5 cm layers (which were measured to check the sampling procedure) were below the detection limit ( $0.5 \mu\text{g dm}^{-3}$ ). As shown by Fig. 5, the amount of ethoprophos in soil decreased drastically in the first few weeks: at 22 days after application only about 50% was left. It is likely that this was not due to transformation within the soil but to some loss process at the soil surface. The ethoprophos concentration profiles measured after 103, 278 and 474 days (Fig. 6) show that the highest concentrations were always found in the top layer (0–4 cm). Only low concentrations penetrated to below 20 cm depth. After 474 days (i.e., at the end of the study) concentrations below 30 cm depth were always below the detection limit of  $0.2 \mu\text{g dm}^{-3}$ .

At 1 day after spraying the average recovered mass of bentazone was  $0.63 \text{ kg ha}^{-1}$  with a SD of  $0.04 \text{ kg ha}^{-1}$ . Correction for the recovery of 86%, results in an average areic mass of  $0.73 \text{ kg ha}^{-1}$  which is about 90% of that calculated to be applied. This figure is almost identical to that found for ethoprophos. Almost all bentazone was found in the top 0–4 cm layer after 1 day: the concentration in the 4–7.5 cm layer was on average only 0.5% of the concentration in the 0–4 cm layer. All concentrations in the layers between 7.5 and 30 cm depth sampled after 1 day were below the detection limit. The bentazone concentration profile measured after 103 days (Fig. 7) shows that bentazone penetrated to

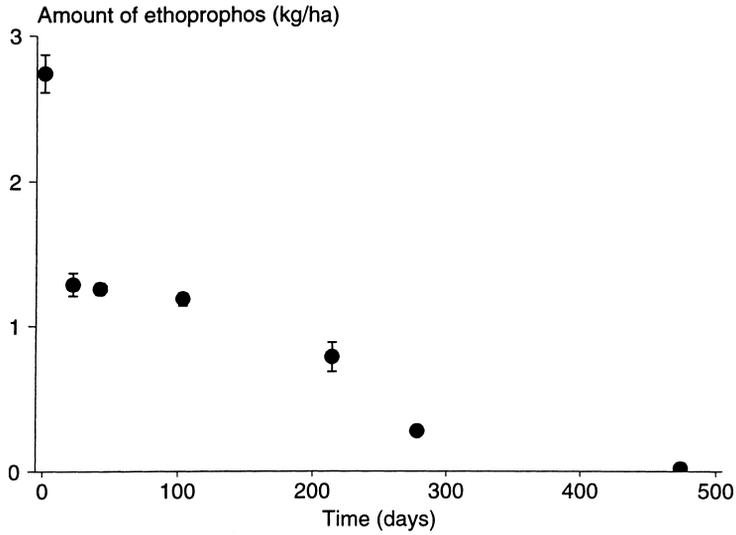


Fig. 5. Areic mass of ethoprophos in soil as a function of time as measured at the experimental field. Time zero corresponds with 0.00 h at 23 November 1990. Points are averages and bars the standard deviation of the average.

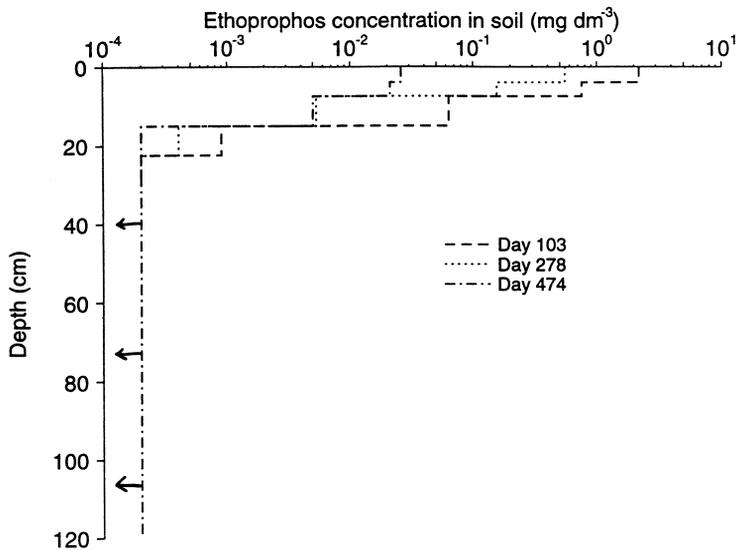


Fig. 6. Average concentration of ethoprophos as a function of depth as measured at the experimental field at 103, 278 and 474 days after application. Concentrations in the 30–45, 45–60, 60–90 and 90–120 cm layers were only measured after 474 days and were all below the detection limit of  $2 \times 10^{-4} \text{ mg dm}^{-3}$  as indicated by the arrows.

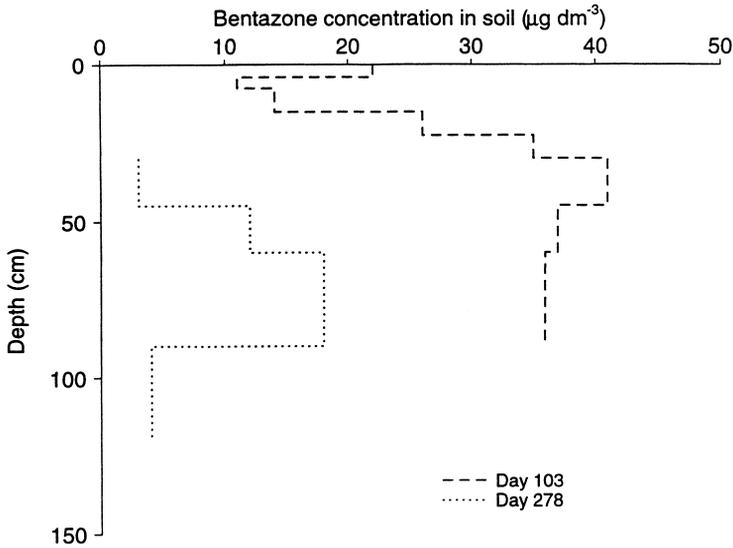


Fig. 7. Average concentration of bentazone as a function of depth as measured at the experimental field at 103 and 278 days after application.

about 90 cm depth at a comparatively high concentration in soil (about  $35 \mu\text{g dm}^{-3}$ ). The profile after 278 days shows a peak in the 60–90 cm layer. In the profile after 474 days, the average bentazone concentration in the whole 0–120 cm layer was below the detection limit of  $1\text{--}2 \mu\text{g dm}^{-3}$ . Comparison of Figs. 4, 6 and 7 shows that bentazone is less mobile than bromide but much more mobile than ethoprophos.

## 5. Results of the laboratory studies

The results of the measurements of the pF-curve and the unsaturated hydraulic conductivity were fitted using the RETC optimisation programme (van Genuchten et al., 1991) as described by van den Bosch and Boesten (1994). Results for the pF curves in Fig. 8A show that the curves for the black top layer (10–18 cm sample) and for the brown layer (45–53 cm sample) were remarkably similar. Between 10 and 100 cm matric head, the volume fraction of liquid for the brown layer is even higher than for the black layer. This is not consistent with the moisture profiles sampled in wet periods (after 1, 103 and 474 days) shown in Fig. 3 these profiles show a sharp drop around 30 cm depth (which is about the transition between the black and the brown layer as described in Section 2.1). The inconsistency may be attributable to spatial variability in soil hydraulic properties: the samples for the soil hydraulic properties were taken from one pit whereas the soil moisture profiles are averages of 16 sampling spots. The hydraulic conductivity relationships of the three layers almost coincided (Fig. 8B).

The results of the incubation study with ethoprophos and soil material from the 0–25 cm layer show that temperature had a distinct effect on the transformation rate

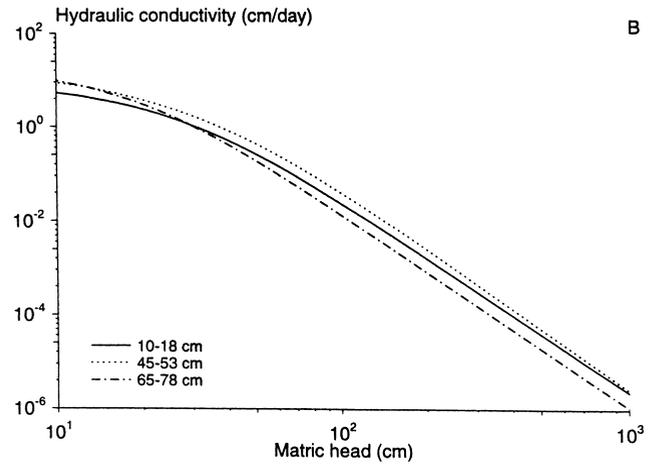
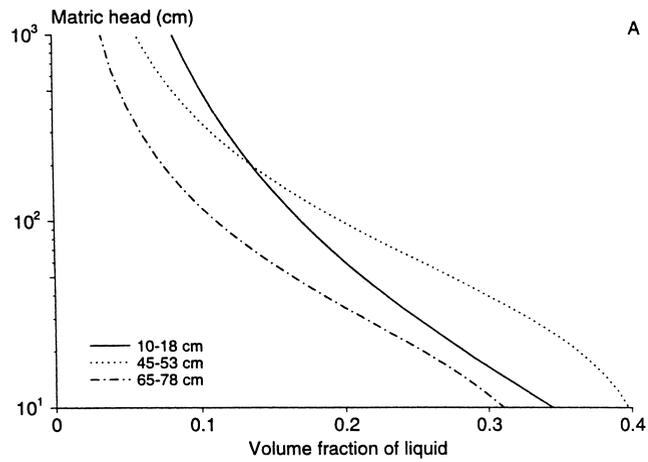


Fig. 8. Hydraulic characteristics measured in the laboratory for the 10–18, 45–53 and 65–78 cm soil layers sampled from one pit in the experimental field.

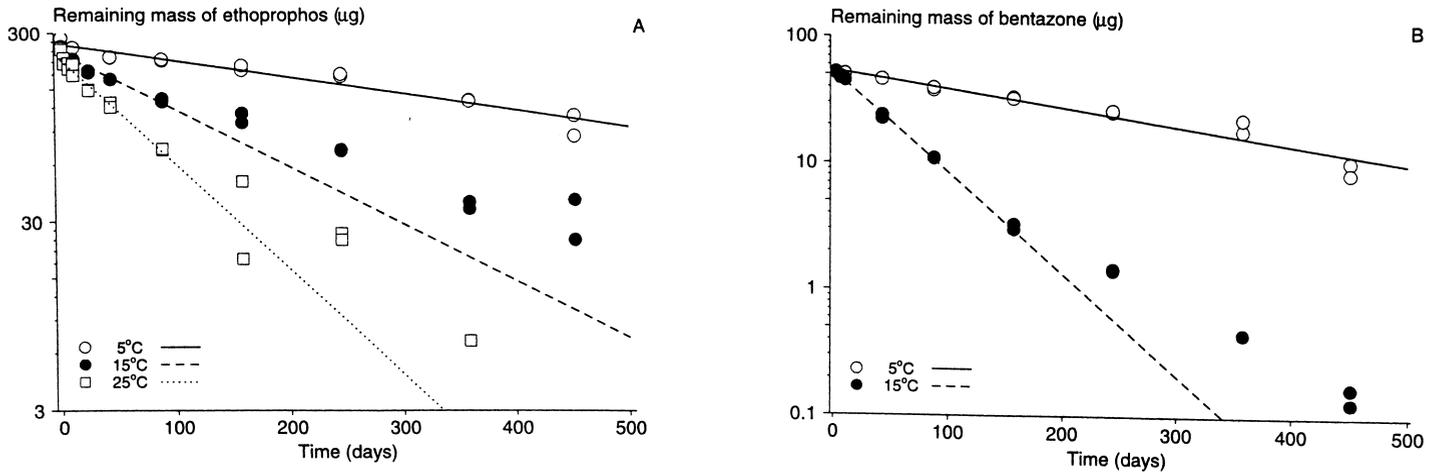


Fig. 9. Remaining mass of ethoprophos (Part A) and bentazone (Part B) as a function of incubation time as measured in laboratory incubations at different temperatures with soil sampled from the 0–25 cm layer at the experimental field. The points are measurements and the lines are fitted assuming first-order kinetics (including only measurements for times shorter than 100 days for 15 and 25°C).

(Fig. 9A). The transformation at 5°C proceeded very slowly. We observed a similar slow decline in the field between 22 and 100 days (see Fig. 5) when soil temperatures did not differ much from 5°C (see Fig. 1). The results at 15 and 25°C indicate that the transformation rate slowed down somewhat between 100 and 400 days; this is probably attributable to a decreasing microbial activity in the incubation systems (Anderson, 1987). Fig. 9B shows that the transformation rate of bentazone in soil material from the 0–25 cm layer proceeded very slowly at 5°C (comparable to the rate of ethoprophos at 5°C). However, the transformation rate of bentazone at 15°C proceeded much faster than at 5°C. At 15°C the transformation rate slowed down somewhat between 100 and 400 days as was also the case with ethoprophos at 15 and 25°C.

The results of all transformation rate studies with material from the 50–100 and 100–200 cm layers could be reasonably well described with first-order kinetics although there was considerable variability between results obtained for ethoprophos at the different sampling times. The first-order rate coefficient of ethoprophos was 0.0011 per day with an SD of 0.0004 per day for the 50–100 cm layer and  $0.0019 \pm 0.0003$  per day for the 100–200 cm layer. The transformation study with bentazone and the 50–100 cm layer showed no significant decrease during the incubation period of over 400 days (rate coefficient was  $0.00009 \pm 0.00015$  per day). The rate coefficient found for bentazone in the material from the 100–200 cm layer was  $0.0072 \pm 0.0001$  per day. As indicated in Table 1, the properties of the 50–100 and 100–200 cm layers were very similar. The difference in bentazone transformation behaviour is, therefore, probably attributable to the difference in the incubation procedure: the 50–100 cm layer was incubated under unsaturated conditions whereas the 100–200 cm layer was incubated at water-saturated conditions.

The sorption isotherms for ethoprophos as shown in Fig. 10A showed an increase of sorption with increasing temperature. This is not common for pesticides and soil (Calvet et al., 1980) although e.g. Dao and Lavy (1978) found it also for atrazine. We fitted Freundlich isotherms using linear regression with the restriction of an equal value of the Freundlich exponent for both temperatures. The results in Fig. 10A indicate that the description was acceptable at both temperatures. The fitted Freundlich coefficient at 25°C was about 40% higher than that found at 5°C. The sorption isotherms with bentazone (Fig. 10B) show a large scatter at both temperatures. As described by Boesten (1990), the experimental error in sorption coefficients is controlled by the dimensionless product of the solid–liquid ratio and the sorption coefficient. In these measurements this product was about 0.2 which indicates low accuracy. The results imply that bentazone sorption was very weak. Fig. 10B shows that the differences between the two temperatures were not significant given the large experimental error.

## 6. Recommended values for pesticide model input parameters

### 6.1. Theory

We define here the equations and the relevant pesticide parameters. For the relationship between soil temperature and the first-order pesticide transformation rate coefficient,  $k$

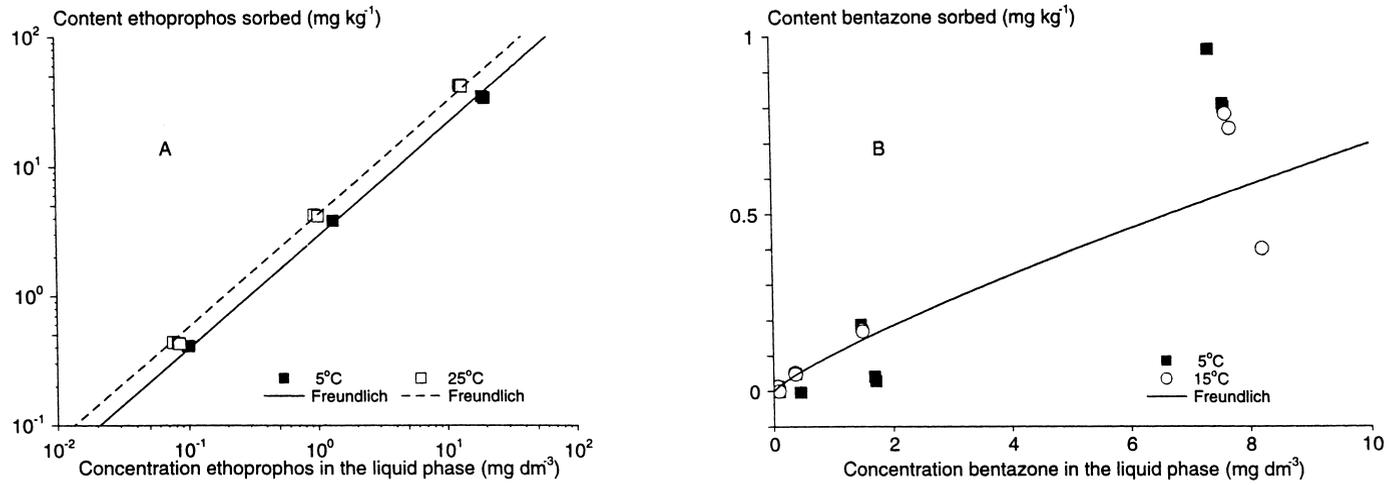


Fig. 10. Sorption isotherms as measured for ethoprophos at 5 and 25°C (Part A) and bentazone at 5 and 15°C (Part B) using soil sampled from the 0–25 cm layer of the experimental field. Points are measurements and lines are fits of a Freundlich isotherm (for Part A equal Freundlich exponents for the two temperatures are assumed and for Part B only one isotherm is fitted to all measurements).

(per day), two equations are considered: the first is the Arrhenius equation used by many models:

$$k = k_{\text{REF}} \exp \left[ - \left( \frac{E_A}{R} \right) \left( \frac{1}{T} - \frac{1}{T_{\text{REF}}} \right) \right] \quad (1)$$

in which  $k_{\text{REF}}$  is the rate coefficient at the reference temperature  $T_{\text{REF}}$ ,  $E_A$  is the activation energy ( $\text{J mol}^{-1}$ ),  $R$  is the gas constant ( $8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is absolute temperature (K). The second is the more simple exponential equation used by PESTLA 2.3 and MACRO:

$$k = k_{\text{REF}} \exp (\gamma(T - T_{\text{REF}})) \quad (2)$$

in which  $\gamma$  is a parameter ( $\text{K}^{-1}$ ). This equation is mathematically identical to the  $Q_{10}$  equation used by e.g., PELMO:

$$k = k_{\text{REF}} (Q_{10})^{\Delta T} \quad (3)$$

in which  $Q_{10}$  is the parameter and  $\Delta T$  is defined as  $(T - T_{\text{REF}})/10$ . Combining Eqs. (2–3) results in the relationship

$$Q_{10} = \exp (10\gamma) \quad (4)$$

For the description of the pesticide sorption isotherms, both the Freundlich and the linear sorption isotherm are used. The following Freundlich equation is used:

$$X = K_F C_{\text{REF}} \left( \frac{C}{C_{\text{REF}}} \right)^N \quad (5)$$

in which  $X$  is content sorbed ( $\text{mg kg}^{-1}$ ),  $K_F$  is the Freundlich coefficient ( $\text{dm}^3 \text{ kg}^{-1}$ ),  $C$  is the concentration in liquid phase ( $\text{mg dm}^{-3}$ ),  $C_{\text{REF}}$  is a reference value of  $C$  set at  $1 \text{ mg dm}^{-3}$  and  $N$  is the Freundlich exponent. The equation for the linear sorption isotherm is:

$$X = K_L C \quad (6)$$

in which  $K_L$  is the slope of the linear isotherm ( $\text{dm}^3 \text{ kg}^{-1}$ ).

The Henry coefficient,  $K_H$ , (defined as the mass concentration in gas phase divided by the mass concentration in liquid phase) can be estimated as the quotient of the concentration in the gas and liquid phases at saturation (so based on the saturated vapour pressure and the water solubility). Using the gas law,  $K_H$  can be estimated from:

$$K_H = \frac{MP}{SRT} \quad (7)$$

in which  $M$  is the molar mass ( $\text{kg/mol}$ ),  $P$  is the saturated vapour pressure (Pa) and  $S$  is water solubility ( $\text{kg m}^{-3}$ ).

## 6.2. Recommended model input values

### 6.2.1. Pesticide dosages

As described before, the concentrations of bentazone and ethoprophos presented were not corrected for recoveries (which were always above 85%). For bentazone, the dosage is based on the amount recovered at 1 day after spraying (so  $0.63 \text{ kg ha}^{-1}$ ). For ethoprophos, we distinguish between models that include simulation of volatilisation and between models that do not include this process. For models including volatilisation, the recommended dose is  $3.0 \text{ kg ha}^{-1}$  (based on the nominal dose of  $3.35 \text{ kg ha}^{-1}$  multiplied with the recovery percentage of 89%). For models without volatilisation, the recommended dose is  $1.33 \text{ kg ha}^{-1}$  (estimated from  $1.29 \text{ kg ha}^{-1}$  recovered after 22 days and  $1.26 \text{ kg ha}^{-1}$  recovered after 42 days). So we interpret the rapid loss in the first 22 days to be the result of volatilisation. This is based on a field experiment done in 1993 with the same soil in which substantial volatilisation of ethoprophos was measured via air sampling (Bor et al., 1995). The results in Fig. 9A show that transformation in soil cannot explain the rapid loss during the first 22 days in the field shown in Fig. 5. Admittedly, the field experiment by Bor et al. (1995) does not prove quantitatively that the rapid initial loss in our field experiment is solely the result of volatilisation: also other processes taking place in the top millimetre of the soil may have played a role.

### 6.2.2. Transformation rates

In most models, the transformation rate depends on soil moisture content, volume fraction of liquid or matric head. Therefore, these three quantities are estimated here for the studies. As described before, the moisture content in the incubation of the 0–25 cm layer was  $0.15 \text{ kg kg}^{-1}$ ; we can relate this to the moisture retention curve for the 10–18 cm layer shown in Fig. 8A. The dry bulk density for the 10–18 cm layer is estimated at  $1.36 \text{ kg dm}^{-3}$  so  $0.15 \text{ kg kg}^{-1}$  corresponds with a volume fraction of liquid of 0.20. This value corresponds with an estimated matric head of about 60 cm. Similarly the moisture content in the incubation of the 50–100 cm layer was  $0.105 \text{ kg kg}^{-1}$  which corresponds with a matric head of 50 cm (using an estimated bulk density of  $1.67 \text{ kg dm}^{-3}$ ). Note that these estimates of the matric head during the incubation are rough because soil structure during the incubation study is different from that in the field due to the mixing of the soil in the lab. The 100–200 cm layer was incubated under water-saturated conditions. The moisture content was  $0.27 \text{ kg kg}^{-1}$  which corresponds with a volume fraction of liquid of 0.46.

From the laboratory studies with ethoprophos and the soil from the 0–25 cm layer, the following first-order rate coefficients and corresponding half-lives were derived: 0.002006 per day and 349 days at  $5^\circ\text{C}$ , 0.006938 per day and 100 days at  $15^\circ\text{C}$ , 0.012786 per day and 54 days at  $25^\circ\text{C}$ . These values were obtained using linear regression of the logarithm of the remaining mass against time (see Fig. 9). Incubation times longer than 100 days were ignored for the 15 and  $25^\circ\text{C}$  incubations because the decrease slowed down at longer times which is probably attributable to a decreased microbial activity (Anderson, 1987). Fitting the Arrhenius equation (Eq. (1)) to the above data via linear regression after logarithmic transformation gave an  $E_A$  value of

64.0 kJ mol<sup>-1</sup> and half-lives of 76.4 days at 20°C and of 193.4 days at 10°C. Fitting the exponential equation (Eq. (2)) resulted in  $\gamma = 0.0926 \text{ K}^{-1}$  and in half-lives of 77.6 days at 20°C and of 195.9 days at 10°C. Using Eq. (4) results in a  $Q_{10}$  of 2.52. For models that have no temperature-dependent transformation rate, we suggest to use the half-life corresponding with the average soil temperature at 2.5 cm depth over the whole experimental period (i.e., is 8.7°C). The corresponding half-life of ethoprophos using Eq. (1) equals 219 days.

As indicated before, the first-order transformation rate coefficients derived from the laboratory studies with ethoprophos and the soil from the 50–100 and 100–200 cm layers had high variation coefficients (17–36%). These high values are attributable to large scatter in the data which is probably due to systematic differences between recovered amounts at the different sampling times (initial content was as low as 12  $\mu\text{g kg}^{-1}$ ). It is, therefore, not meaningful to use different half-lives for the two layers. So the averaged rate coefficient of 0.00147 per day is recommended which corresponds with a half-life of 472 days. Note that this value was measured at 10°C. It is recommended to use the values from the 0–25 cm layer up to 32 cm depth and to interpolate linearly between 32 and 50 cm depth.

From the laboratory studies with bentazone and the soil from the 0–25 cm layer, a half-life of 206 days was derived at 5°C and of 37.6 days at 15°C. The variation coefficient of the rate coefficient at 5°C was only 7%. These values were obtained using linear regression of the logarithm of the remaining mass against time. Incubation times longer than 100 days for the 15°C incubation were ignored as for ethoprophos (including the longer incubation times would have resulted in 53.0 days at 15°C so 41% higher). On the basis of the CV of 7% we conclude that the rate coefficient at 5°C can be derived with sufficient accuracy from the measured decline. The bentazone concentration profile measured after 103 days implies that 11% of the dose is present in the 0–30 cm layer and that 36% of the dose is present in the 30–90 cm layer. So in the first 103 d, the areic mass of bentazone in the 0–30 cm layer decreased with 89% (due to both leaching and transformation). During the first 103 days the average air temperature was 2.6°C (derived by averaging the daily minimum and maximum temperatures). The average soil temperature at 2.5 cm depth over this period was 1.9°C and the range of the daily average of soil temperatures over this period was from -7 to +8°C. So during the period in which the areic mass in the 0–30 cm layer declined by 89%, average air and soil temperatures were close to the 5°C used in the incubation experiment. Therefore, the incubation at 5°C is the basis for the estimation of the parameters.

For models that have a temperature-dependent transformation rate, it is proposed to use the half-life of 206 days at 5°C in combination with an Arrhenius activation energy of 54 kJ mol<sup>-1</sup> (the average from a recent literature survey by FOCUS Soil Modelling Workgroup, 1997). This results in half-lives of 136.0 at 10°C, 91.3 at 15°C and 62.2 days at 20°C. The  $Q_{10}$ -value for the reference temperature of 20°C is 2.220. The half-life measured at 15°C (37.6 days) is not used because it results in an extremely high activation energy (which in most models then also would apply to deeper soil layers). For models in which the transformation rate is constant with temperature, the half-life of 206 days is recommended because the soil temperature in the most relevant period was close to 5°C.

As described before, there was no significant decrease in the laboratory study with bentazone and the soil from the 50–100 cm layer over a 400-days period. Therefore, we suggest to assume no transformation in this layer. From the laboratory study with the soil from the 100–200 cm layer, a first-order rate coefficient of 0.0072 per day (half-life of 96.1 days) was derived. Note that this value applies to 10°C. As for ethoprophos, it is recommended to use the values from the 0–25 cm layer up to 32 cm depth and to interpolate linearly between 32 and 50 cm depth.

### 6.2.3. Pesticide sorption parameters

The results of the sorption isotherm measurements at 5 and 25°C were fitted to the Freundlich equation with the restriction that the Freundlich exponent should be equal (using linear regression after log–log transformation). The fitted lines are shown in Fig. 10A. The  $N$  value was 0.866 and  $K_F$  was 2.87 dm<sup>3</sup> kg<sup>-1</sup> at 5°C and 4.23 dm<sup>3</sup> kg<sup>-1</sup> at 25°C. During the incubations for the transformation rate measurements with the 0–25 cm layer, the soil pore water concentration were measured (see Boesten and van der Pas, 1999). It can be expected that the concentrations in the soil pore water should correspond with the sorption isotherm in the first weeks of the incubation study (later, increasing sorption with time will lead to lower pore water concentrations than expected on the basis of the isotherms). Comparison of measured pore water concentrations with those expected from the sorption isotherms showed that there was good correspondence for 25°C. However, for 5°C the estimated pore water concentrations were much higher than the measured ones. So far there is no explanation for this inconsistency. The pore water concentrations measured at 5°C corresponded well with the sorption isotherm of 25°C. Therefore, we propose to ignore the sorption isotherm measured at 5°C and to use the  $K_F$  value from 25°C (i.e., 4.23 dm<sup>3</sup> kg<sup>-1</sup>). This corresponds with a  $K_{OM}$  value of 86 dm<sup>3</sup> kg<sup>-1</sup> and a  $K_{OC}$  value of 185 dm<sup>3</sup> kg<sup>-1</sup>.

The amount ethoprophos that penetrated into the soil was estimated at 1.33 kg ha<sup>-1</sup>. This corresponds with a total concentration of about 3 mg dm<sup>-3</sup> over a depth of 4 cm. Using  $K_F = 4.23$  dm<sup>3</sup> kg<sup>-1</sup> and  $N = 0.866$ , a total concentration of 3 mg dm<sup>-3</sup> implies a concentration in the liquid phase of about 0.5 mg dm<sup>-3</sup>. This is sufficiently close the  $C_{REF}$  value of 1 mg dm<sup>-3</sup> so for models assuming a linear isotherm it is recommended to use also  $K_L = 4.23$  dm<sup>3</sup> kg<sup>-1</sup> (and  $K_{OM} = 86$  dm<sup>3</sup> kg<sup>-1</sup> and  $K_{OC} = 185$  dm<sup>3</sup> kg<sup>-1</sup>).

In view of the large scatter in the data as shown in Fig. 10B, the results from the sorption isotherm measurements with bentazone at 5 and 15°C were combined. Furthermore, sorption points with contents sorbed below zero were ignored. Linear regression after log–log transformation resulted in  $N = 0.82$  and  $K_F = 0.105$  dm<sup>3</sup> kg<sup>-1</sup> at  $C_{REF} = 1$  mg dm<sup>-3</sup>. The corresponding  $K_{OM}$  is 2.14 dm<sup>3</sup> kg<sup>-1</sup> and the corresponding  $K_{OC}$  is 4.59 dm<sup>3</sup> kg<sup>-1</sup>.

The bentazone dose and sorption parameters imply that the concentrations in the liquid phase in the top layer in the first months after application are roughly in the range 0.1–1 mg dm<sup>-3</sup>. So for models using a linear isotherm, a  $K_L$  value of 0.105 dm<sup>3</sup> kg<sup>-1</sup> is recommended.

The recommended sorption isotherm parameters are based on measurements in soil–water suspensions with an equilibration time of 24 h. Therefore, these parameter values do not include any long-term sorption process.

#### 6.2.4. Henry coefficient

An estimate of the Henry coefficient for ethoprophos is relevant for models that include volatilisation and transport in the vapour phase. Bentazone will be present as an anion in the soil solution in view of its  $pK_A$  of 3.2 (Abernathy and Wax, 1973) so the Henry coefficient is estimated to be zero. Tomlin (1994) gives for ethoprophos the following values for the parameters in Eq. (7):  $M = 0.2423 \text{ kg mol}^{-1}$ ,  $S = 0.7 \text{ kg m}^{-3}$  at  $20^\circ\text{C}$  and  $P = 0.0465 \text{ Pa}$  at  $26^\circ\text{C}$ . With Eq. (7) this gives  $K_H = 6.5 \times 10^{-6}$ . This is a value for  $20\text{--}26^\circ\text{C}$ . The Henry coefficient is only relevant in the first 2 weeks after application: then the range of daily maximum air temperatures was  $3\text{--}8^\circ\text{C}$  so roughly  $15\text{--}20^\circ\text{C}$  lower. It can be expected that the  $K_H$  decreases roughly a factor two per decrease of  $10^\circ\text{C}$  (approximately found by Leistra, 1970, for 1,3-dichloropropene). Dividing the  $K_H$  value by four and rounding off gives a recommended value of  $2 \times 10^{-6}$ .

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