Comportement des produits phytosanitaires dans les fossés

Fate and Behaviour of Pesticides in Farm Ditches

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Abstract: A field study has been set up to study the transport of pesticides through ditches draining land in cereal production. This paper shows data for three pesticides in two ditches. Isoproturon and diflufenican loads over a drainage season were reduced by between 30% and 60% over a distance of 400m. Laboratory tests showed that both isoproturon and diflufenican would sorb to bed sediments and that desorption was not fully reversible. This indicates that the loss in the ditch was probably due to sorption to the ditch sediments. Propyzamide, however, showed a decrease in the load transported for the first two runoff events after its application, however subsequent events showed a gain with no net loss over the 5 events studied. Within these events there was an initial loss of propyzamide followed by a gain. Laboratory sorption/desorption tests are to be carried out for propyzamide.

Keywords: Isoproturon, diflufenican, propyzamide, ditches, sorption, runoff

Mots-clés: Isoproturon, diflufenican, propyzamide, fossés, sorption, ruissellement

1. Introduction

Extensive research has been carried out on pesticide losses from plots and fields. The processes that lead to pesticide runoff are reasonably well understood although they have proved too complex to model reliably at present. Farm ditches are an important part of the surface water drainage network, linking pesticide runoff from fields to the permanent watercourse network. The amount of pesticide passing through ditches may be modified by a number of physical, biological and chemical processes: sorption (to sediments or plants), volatilization, uptake (by plants and animals), degradation (biotic and abiotic). These in-ditch processes may play an important role in reducing the loads of pesticides reaching rivers used for water supply. This paper describes results from a field study where an attempt has been made to quantify the losses of a range of pesticides as they pass along two farm ditches.
2. Methods

2.1 Field Site

The study site is located at the Oxford university farm at Wytham, situated 10 km to the west of Oxford, UK. The predominant soil type is heavy clay from the Denchworth series. The farm practices mixed agriculture based on sheep, beef and cereal production. The cereals follow a 4-year rotation of 3 winter-sown cereals followed by winter oil seed rape.

At Wytham the aim is to study the behaviour of pesticides in ditches arising from runoff from fields receiving applications in the course of normal agricultural production. Two ephemeral ditches have been selected for study (Figure 1). The ditches are about 1 m wide at the top narrowing to ~0.3 m at their base. The study section for Ditch A is 150 m long and 400 m long for Ditch B. The ditches are fed by a combination of subsurface drains, subsurface lateral flow and some overland flow, although the latter is reduced at certain locations by a 3 m grassed buffer strip along the edge of the ditch.

![Diagram of Wytham field site showing the locations of the sampling sites on the two ditches being studied](image)

*Fig. n° 1 : Wytham field site showing the locations of the sampling sites on the two ditches being studied*
2.2 Flow measurement

Flow measurements have been made at 15 minute intervals at sites A1, A3, B1 and B3 (Figure 1). At sites A1, A3 and B1, flow was measured using pre-formed flumes (Scottish Environmental Protection Agency, Edinburgh) embedded in the beds of the ditches during the early spring of 1999. Figure 2 shows a detail from the flume at site A1. At site B3 flowrate was measured using an existing V-notch weir installed as part of the UK Environmental Change Network. For both flow devices, the flow over the weir can be calculated from the depth of water above the weir using standard rating curves. Depth data from the pressure transducers were stored on solid-state loggers, which were downloaded each week.

Fig. n° 2 : Pre-formed flume structure imbedded in the ditch at site A1

2.3 Sampling

A two-level approach to sampling was taken: routine sampling and event sampling. Routine samples were taken regularly from the six sites both before and after the applications of the target pesticides were made. The water samples were taken in 1-litre, brown glass bottles and stored at 4°C prior to analysis. Bed-sediment samples were taken each month from each of the six sites. The samples were taken by carefully removing the top 2 cm of the bed sediment using a metal trowel and placing it in a polythene bag. The samples were kept frozen at –18°C prior to analysis.
Event samples were taken to study the dynamics of pesticide transport within the ditch during periods of high flow. During rainfall not only will pesticides be transported from the surrounding fields to the ditches, but also there is scope for re-mobilisation of pesticides sorbed to bed-sediments. Automatic samplers at sites A1, A3, B1 and B3 were linked to the solid-state data loggers and were programmed to take a series of samples when the level of water in the ditch rose above a specific value. Samples were collected every 15 minutes for the first 6 samples and then half hourly or hourly there after. The samplers ceased taking samples when the level fell below the trigger value. Samples were recovered from the field as soon as was practicable, usually within 48 hours and stored at 4°C prior to analysis. Figure 3 shows an automatic sampler on the bank at site A1.

![Automatic sampler at site A1](image)

*Fig. n° 3 : Detail of an epic automatic sampler at site A1 showing the arrangement of bottles within the base. The aluminium box contains the solid-state logger that controls the initiation of the sampling programme.*

2.4 Pesticides studied

In order to separate processes occurring within the ditch from diffuse pesticide inputs along the length of the ditch, only pesticides applied to land draining to points above the upper most sampling point were studied. This paper describes applications of 3 pesticides, isoproturon, diflufenican (to winter wheat) and propyzamide (to winter oil seed rape).

- **Ditch A**: Propyzamide at 1.4 kg a.i./ha on 26th October 2000
- **Ditch B**: Isoproturon at 1.5 kg a.i./ha on 21st November and 0.61 kg a.i./ha on 23rd November 1999
  - Diflufenican at 60 g a.i./ha on 23rd November 1999
These pesticides have contrasting properties (Table 1).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Propyzamide</th>
<th>Isoproturon</th>
<th>Diflufenican</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour pressure (mPa)</td>
<td>0.058</td>
<td>0.0033 (20°C)</td>
<td>0.07 (30°C)</td>
</tr>
<tr>
<td>Koc (l/kg)</td>
<td>800</td>
<td>120</td>
<td>1990</td>
</tr>
<tr>
<td>DT50 (days)</td>
<td>60</td>
<td>12-32</td>
<td>175-294</td>
</tr>
</tbody>
</table>

*Table n° 1: Properties of the herbicides studied in the field. Koc and DT50 values refer to measurements made in soil.*

2.5 Analysis

2.5.1 Pesticides in water

Samples were filtered through pre-weighed and pre-dried 0.45 µm glass fibre filters and the filtrates were extracted by C18 solid phase cartridge. The cartridges were eluted with acetonitrile and analysis was by gas chromatography with mass spectrometer detection operating in single ion mode for diflufenican and by high-pressure liquid chromatography with UV detection for isoproturon. The detection limit was 0.03 µg/l for both pesticides. Propyzamide was not extracted but was injected directly into an HPLC with detection by MS in single ion mode. The detection limit was 1 µg/l.

2.5.2 Sediment Samples

Supercritical-fluid extraction (SFE) of ca 1 g of material was performed using a Dionex system (SFE-703) with Co-Solvent Addition Module, using SFC/SFE grade CO2, pesticide-grade methanol and a Jun-Air 18-50 compressor. The extracts were collected in 20 ml of ethyl acetate. The volume was reduced to 1.5 ml using pure nitrogen. Blank samples with no sediment material were included in the sample batch. The compounds were analysed by gas chromatography (GC) with mass spectrometer detection (Perkin Elmer TurboMass) in electron ionisation mode. The GC column was a 30 m x 0.25 mm PE-5MS. The analysis was conducted in single-ion mode (SIM), with quantification from the abundance of the base ion and confirmation by at least one qualifier ion.
3. Results and Discussion

3.1 Isoproturon and Diflufenican – Regular Samples

Samples were collected on a weekly basis and were combined with the instantaneous flow on that day to produce mass flows of IPU and DFF at the upstream and downstream sites. These instantaneous values were converted into a mass per 15 minutes, the flow-sampling interval. The data for IPU are presented in Figure 4. The most significant masses of IPU were found in the two samples taken immediately after the pesticide application and the mass loss along the ditch is most significant in these samples. Later on the mass loads transported are low and there is generally a gain in IPU load down the ditch.

The sorption coefficients (K_d) measured in the laboratory for IPU (3.7 kg/l) and DFF (17.4 –23.2 kg/l) to sediments from Ditch B showed that there was potential for loss of these chemicals through binding to the sediments. Measurements of sediment samples taken from the ditches showed concentrations of IPU of up to 477 µg/kg and DFF concentrations of up to 1642 µg/kg. Measurable levels (<10 µg/kg) were only found for 2 months after the application. There seems to be two phases to the transport of IPU (and also DFF). Initially there is sorption if IPU from the pesticide-rich water, followed by release of IPU from the sediments when concentration in the water column reduces. There is likely to be degradation of pesticide in the sediments over the season, but this has not been studied.

The 15-minute load values can, with a great deal of caution, be interpolated to give pesticide mass balances over the season. The need for caution arises from the very rapid response of ditch pesticide concentrations to rainfall events and the fact that weekly sampling will not reflect well these short-lived event concentrations. Table 2 shows maximum and minimum estimates of the IPU and DFF loads at the top and bottom of ditch B. The maximum estimate comes from assuming a linear interpolation between weekly values. The minimum estimate comes from assuming that a missing concentration value for a week is best characterized by the lower of the two adjacent values.

For both IPU and DFF there is a clear reduction in the mass of pesticide leaving Ditch B compared to that entering the ditch. For IPU the reduction is 61% assuming the largest mass estimates and 44% assuming the smallest mass load estimates. The corresponding figures for DFF are 57% and 29%. These figures show that the ditch is greatly reducing pesticide concentrations in runoff water from treated fields in excess of that which might be expected by dilution alone.
Fig. n° 4: Mass of isoproturon transported at the top (B1) and bottom (B3) of the ditch. The numbers on the bars show the concentration of isoproturon.

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Site</th>
<th>Maximum (g)</th>
<th>Minimum (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IPU</td>
<td>B1 (top)</td>
<td>334</td>
<td>118</td>
</tr>
<tr>
<td>IPU</td>
<td>B3 bottom</td>
<td>129</td>
<td>66</td>
</tr>
<tr>
<td>DFF</td>
<td>B1 (top)</td>
<td>2.90</td>
<td>1.01</td>
</tr>
<tr>
<td>DFF</td>
<td>B3 (bottom)</td>
<td>1.24</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Table n° 2 : Mass balances for IPU and DFF along Ditch B over Autumn 1999 to Spring 2000

3.2 Propyzamide – Event samples

Short interval sampling carried out over rainfall events showed a pulse of Propyzamide passing down the ditch (figure 5). The flow rates at the top and bottom of the ditch are similar but the loads of propyzamide carried are much larger at the top site early in the event. Overall there is a net loss of propyzamide.
over the 7 hours for which he event lasts. At this short time scale these data show a similar pattern to the regular samples taken for IPU and DFF; at the beginning of the event there is loss of propyzamide followed by a gain later on. The event shown was the first to occur after application (2 days before). The second event also showed a net loss of propyzamide, however, subsequent events showed a different pattern in which there was an overall gain of pesticide over the reach; these events are summarized in table 3.

<table>
<thead>
<tr>
<th>Date</th>
<th>Mass at top (g)</th>
<th>Mass at bottom (g)</th>
<th>Loss/(gain) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28/10/2000</td>
<td>13.3</td>
<td>12.1</td>
<td>1.2</td>
</tr>
<tr>
<td>29/10/2000</td>
<td>13.9</td>
<td>13.2</td>
<td>0.7</td>
</tr>
<tr>
<td>31/10/2000</td>
<td>0.8</td>
<td>0.9</td>
<td>(0.1)</td>
</tr>
<tr>
<td>2/11/2000</td>
<td>4.1</td>
<td>6.6</td>
<td>(2.5)</td>
</tr>
<tr>
<td>11/11/2000</td>
<td>6.4</td>
<td>6.5</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Total</td>
<td>38.5</td>
<td>39.3</td>
<td>(0.8)</td>
</tr>
</tbody>
</table>

Table n°3: Propyzamide loads calculated at the top and bottom of ditch A for 5 rainfall events.

Within the errors associated with calculating the loads there was an approximate equality between the amounts of pesticide at the top and bottom of the ditch showing that for propyzamide the ditch does not reduce the pesticide runoff loads. When propyzamide was studied on ditch B in 1998/99 routine samples showed there was a reduction in propyzamide concentrations between the top and bottom sites (Williams et al, 1999), but subsequent analysis showed that the loads had not decreased. This overall effect is in contrast to IPU and DFF for which there was net loss of pesticide. The pattern of sorption of pesticide followed by release is however similar.

Analysis of bed sediments from both ditches A and B showed propyzamide had been sorbed, which would suggest that some should have been retained. However, if the sorption is completely reversible then this could account for the observations in the storm events. Further laboratory tests are being carried out to test this. Further event samples and routine samples for propyzamide from this season (2000-01) have been collected, but have not yet been analysed.
4. Conclusions

Pesticide losses were most important in samples taken close to the time of application.

IPU and DFF loads were reduced as they moved through the ditch by between 30 and 60%. The most likely removal process is sorption on to the bed sediments probably followed by degradation.

In high flow events, propyzamide showed the same pattern of initial sorption followed by release. Overall, however, propyzamide was not retained in the ditches, which may indicate a more easily reversible sorption than for IPU and DFF.

Acknowledgements

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