HERBICIDE RUNOFF STUDIES IN AN ARABLE SOIL UNDER SIMULATED RAINFALL

K. MÜLLER, M. TROLOVE, T.K. JAMES and A. RAHMAN
AgResearch, Ruakura Research Centre, Private Bag 3123, Hamilton
Corresponding author: karin.mueller@agresearch.co.nz

ABSTRACT
Runoff potential of five herbicides (acetochlor, atrazine, hexazinone, pendimethalin and terbuthylazine) was investigated on a fallow Hamilton clay loam soil with a 10% slope. Twenty-four hours after the herbicide application, simulated rainfall was applied at three intensities. Sediment amounts and herbicide concentrations were determined in the water phase of runoff samples. Herbicide residues attached to sediment were estimated using K_d-values determined locally for the Hamilton clay loam soil. Pesticide concentrations were the highest in the first runoff samples and decreased exponentially with further rain. Results show that herbicides were primarily transported in their dissolved forms in runoff, and that losses are dependent on the time to runoff and runoff rates. Rainfall intensity had no significant effect on herbicide losses. In all cases losses were <1% of the amounts applied.

Keywords: surface runoff, rainfall simulation, herbicides, environmental fate.

INTRODUCTION
Off-target movement of pesticides is an ecological and human health concern. Understanding the processes, which determine pesticide transport from agricultural fields to water resources, is critical for the safe use of pesticides. Leaching of pesticides to the groundwater has already been documented in New Zealand (Close et al. 1999; Ma et al. 2000). However, not much attention has been paid to pesticide runoff, even though runoff and erosion are considered key factors for nutrient contamination of New Zealand’s waterways (Gillingham & Thorrold 2000). Fox & Wilcock (1988) and Wilcock & Costley (1991) conducted studies in pastoral catchments in the Waikato Region and reported contradictory results on runoff losses of aerially applied herbicides. Basher et al. (1997) noted that intensive horticultural land use in volcanic ash soils combined with frequent high-intensity rainfall caused severe erosion in vegetable production areas such as Pukekohe, but no studies on pesticide export have been reported on arable land in New Zealand.

Chemicals can be exported dissolved in the water phase as well as adsorbed to sediments. Transport processes from the soil to runoff affect pesticide loss, and are influenced by the chemico-physical properties of the compounds, soils, surface conditions and climatic factors. They are therefore site-specific (Zhang et al. 1997).

Microplots, with rainfall simulation, allow controlled replication of rainfall events and initial experimental conditions. Effects of specific parameters, such as rainfall intensity, timing and slope, can be studied in experimental microplots (Battany & Grismer 2000). Use of rainfall simulators enables plots to be exposed to rain immediately after pesticide application and provides information required for validating pesticide transport models (Zhang et al. 1997).

The objective of this study was to investigate the impact of rainfall intensity on herbicide concentration and loads in runoff from an arable soil. A mixture of five commonly used herbicides with diverse properties was applied to an allophanic soil in order to compare their runoff behaviour under identical hydrodynamic conditions.

FIELDS

Three rainfall intensities (70, 88 and 111 mm/h) were applied 24 hours after herbicide application to each of two replicate plots at Gordonton, near Hamilton, during February 2001. The soil was a Hamilton clay loam soil (Typic Hapluhumult) with 3.3% organic C, 42% clay, 34% silt and 25% sand content. The fallow soil was freshly cultivated to simulate pre-planting conditions. Uniform runoff plots (0.5 m by 1 m) with approximately 10% slope were separated by metal borders. A gutter system conveyed runoff to 1-litre bottles installed at the bottom of each plot. The bottles were placed on scales connected to a Campbell CR10X-datalogger, which continuously recorded weight changes. This set-up allowed measurement and calculation of total runoff and runoff rates.

Herbicides covering a range of chemico-physical properties were applied in commercial formulations with a hand held CO$_2$ pressured sprayer with TeeJet 11004TTVP nozzles, operated at 230 kPa and applying 300 litres/ha. Application rates of the products used are summarized in Table 1. The maize herbicides, acetochlor, atrazine, pendimethalin and terbuthylazine, are pre-emergence herbicides. Hexazinone, a herbicide with very high water solubility is used both as pre- and post-emergence treatment. Thus, the experimental herbicide application conditions were realistic.

One day prior to the pesticide application all plots received simulated rainfall of 20 mm/h until the gravimetric water content was 26%. A portable drip-type rainfall simulator was used to simulate rain (Bowyer-Bower & Burt 1989). Each rainfall simulation was stopped after 190 mm of rain. The coefficient of variation of the rainfall under the simulator, measured over a 110 mm square grid at different rainfall intensities, ranged from 10 to 14% with standard deviations of 10 to 25 ml. The raindrop size distribution, the fall height and the velocity of the drops as they hit the soil surface determine the rainfall kinetic energy. The artificial storms of 190 mm (at 70, 88 and 111 mm/h) provided 80% less kinetic energy, but 358% more depth than the natural 10-year, 120-min rainfall event in the area. The surface roughness before and after the rainfall events was measured using a fine chain (1 m length) that exactly follows the contours of the soil surface and then measuring the straight line distance covered by the chain (Saleh 1993).

### Table 1: Some properties and application rates of the herbicides used.

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Trade name</th>
<th>Application rate (g ai/ha)</th>
<th>$K_d$ (litre/kg)</th>
<th>Water solubility (mg/litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetochlor</td>
<td>Roustabout</td>
<td>2520</td>
<td>3.3</td>
<td>223.0</td>
</tr>
<tr>
<td>atrazine</td>
<td>Gesaprim</td>
<td>1500</td>
<td>4.0</td>
<td>100.0</td>
</tr>
<tr>
<td>hexazinone</td>
<td>Velpar DF</td>
<td>7500</td>
<td>0.6</td>
<td>33000.0</td>
</tr>
<tr>
<td>pendimethalin</td>
<td>Stomp 330 E</td>
<td>1980</td>
<td>636.0</td>
<td>0.3</td>
</tr>
<tr>
<td>terbuthylazine</td>
<td>Gardoprim</td>
<td>1500</td>
<td>6.4</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Laboratory methods**

The sediment and water phases of the runoff samples were separated by centrifugation at 1962 RCF (relative centrifugal force) for 10 min. The sediment concentration in the runoff was determined by dividing the dried sediment weight by the volume centrifuged (g/litre).

The herbicides were separated from runoff water by solid phase extraction. The samples were aspirated through $C_{18}$-columns (Alltech, Deerfield, 2.8 ml, 0.5 g $C_{18}$-sorbent material). The adsorbed pesticides were eluted with 1 ml of methanol followed by 2 ml of acetone. The eluent was evaporated under nitrogen and redissolved in 1 ml methanol/purified water (50:50 v/v) for HPLC analysis, which was performed on a Shimadzu LC-6B system with a Luna $C_{18}$ (4.6 mm i.d. by 150 mm) column. The mobile phase was methanol/water (60:40 v/v) at a flow rate of 1 ml/min. Detection was performed by UV absorption at 230 nm (250 nm for acetochlor).
The load of a pesticide contained in the sample collected during a time period was calculated as the product of the average dissolved pesticide concentration and the corresponding runoff volume by triangulation:

\[ I_i = \frac{(C_{d(i)} + C_{d(i)})}{2} (V_{i+1} - V_i) \]  

(1)

Assuming that the partition coefficient \( K_d \) accurately reflects sorption processes during runoff, \( K_d \) values determined locally for the soil were applied to estimate the amount of herbicide transported via sediment (Table 1).

To determine whether significant differences exist between the rainfall intensities, runoff rates and other parameters, the results were analysed using the non-parametric Kruskal-Wallis-Test. Herbicide concentrations were normalised by dividing them with the individual application rates for ease of comparison. All statistical procedures were performed using SAS (release 6.12) at the P<0.05 level.

**RESULTS AND DISCUSSION**

Runoff patterns were similar for all rainfall intensities. Initially, all the rain infiltrated into the soil until the rainfall rate exceeded the soil infiltration capacity. Runoff commenced 12 min (42 mm) after the start of the rainfall with the highest intensity compared to 48 min (100 mm) for the lowest intensity. After initiation, runoff rates increased sharply until they reached a steady state condition. Final runoff rates of 17 and 26 mm/h for the rainfall intensities of 70 and 111 mm/h, respectively, were significantly different. However, the cumulative runoff amounts did not differ significantly after 190 mm of cumulative rainfall (Table 2). Nearly 90% of the rainfall infiltrated into soil on all plots. In general, surface runoff was low because the good soil structure gave a high infiltration capacity. If the soil had been uncultivated and/or covered with vegetation for this experiment, the infiltration rate would have been even higher due to a more stabilised soil aggregate structure and macropores in the rooting zone. All rainfall intensities led to comparable soil surface sealing effects (Table 2). The average sediment loss was less than 1 g/litre due to a lack of kinetic energy of the simulated rain and the good soil structure. The exported mass was low compared to other rainfall simulation studies (e.g. Gouy et al. 1999). Natural rainfall with higher kinetic energy would have produced greater sediment loss.

The worst-case scenarios of the experimental settings resulted in herbicide losses of <1% of the amounts applied (Table 2), which were less than expected (Burgoa & Wauchope 1995). Either the allophanic soil bound the herbicides tightly, or the chemicals were leached into the soil profile before the initiation of runoff. Fox & Wilcock (1988)

**TABLE 2: Details of the simulated rain events and mean herbicide losses after 190 mm rainfall.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Rainfall intensity (mm/h)</th>
<th>70</th>
<th>88</th>
<th>111</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface runoff</td>
<td></td>
<td>16</td>
<td>20</td>
<td>19</td>
</tr>
<tr>
<td>Sediment</td>
<td></td>
<td>99</td>
<td>186</td>
<td>104</td>
</tr>
<tr>
<td>Surface roughness before</td>
<td></td>
<td>15</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>Surface roughness after</td>
<td></td>
<td>8</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>acetochlor (g/ha); (%)</td>
<td></td>
<td>5.8 (0.2)</td>
<td>7.0 (0.3)</td>
<td>9.4 (0.4)</td>
</tr>
<tr>
<td>atrazine (g/ha); (%)</td>
<td></td>
<td>7.0 (0.5)</td>
<td>7.9 (0.5)</td>
<td>10.8 (0.7)</td>
</tr>
<tr>
<td>hexazinone (g/ha); (%)</td>
<td></td>
<td>19.5 (0.3)</td>
<td>21.5 (0.3)</td>
<td>28.9 (0.4)</td>
</tr>
<tr>
<td>pendimethalin (g/ha); (%)</td>
<td></td>
<td>2.7 (0.1)</td>
<td>3.2 (0.2)</td>
<td>2.7 (0.1)</td>
</tr>
<tr>
<td>terbuthylazine (g/ha); (%)</td>
<td></td>
<td>10.4 (0.7)</td>
<td>12.0 (0.8)</td>
<td>15.5 (1.0)</td>
</tr>
</tbody>
</table>

1Values in parentheses represent the loss as a percentage of the amount applied.

applied 2,4,5-T to a watershed (20 – 30% slope), dominated by allophonic soils and in
the first natural storm, which occurred within 8 h after the application, they found only
0.4% of the applied amount in the runoff water.

In this study, the herbicide losses from the three rainfall intensities were not significantly
different. Dissolved herbicides accounted for more than 99.5% of the total loss for all
compounds at all intensities, with the exception of pendimethalin for which 35% of the
loss was estimated to be associated with sediment transport. Losses were governed by
water flux and this is consistent with former research (Jaynes et al. 1999).

For all herbicides and rainfall intensities the highest concentrations were detected in
the first runoff samples, which were collected as soon as the first litre of runoff occurred
(Fig. 1). The total amount of herbicide exported was correlated to the Kd values only for
the compounds pendimethalin and hexazinone, which represent extremely immobile
and mobile pesticides. The behaviour of the other compounds with moderate mobility
and water solubility was unexpected. Terbutylazine was found in higher normalized
concentrations than atrazine, in spite of its higher sorption coefficient. Atrazine was
possibly leached more rapidly with infiltrating water before runoff started. Burgoa &
Wauchope (1995) found a similar relationship.

The highest herbicide concentrations in the runoff water were recorded at the beginning
of the experiment with a maximum concentration of 316 μg/litre hexazinone (Fig. 1).
Mean dissolved hexazinone, acetochlor, atrazine and terbutylazine concentrations
displayed an exponential decline with a linear relationship between the logarithm of the
herbicide concentration and the logarithm of the runoff rate and coefficients of correlation
between 0.80 to 0.95 for all three intensities. The runoff rate played an important role in
the dynamics of the pesticide transport processes. During runoff a continuous extraction
process takes place that supplies soil water with herbicides. The exponential pattern
might be due to rapid initial desorption from sites of multilayer adsorption, followed by slower removal of herbicides from sites with higher bonding energy. The process was influenced by (i) the initial concentration of herbicides in the soil solution and (ii) by the subsequent release of bound herbicides from soil. The delivery rate is expressed in the slope of the regressions. It was more efficient for the herbicides atrazine, terbuthylazine and acetochlor than for the compound hexazinone. This may be because the highly soluble hexazinone has a faster depletion on the soil surface due to rapid leaching. There was substantial movement of water into the tilled soil surface before runoff began.

Pendimethalin, the compound with the lowest water solubility, behaved differently. Variations in the pendimethalin concentrations were small (from 12 to 20 mg/litre) compared to variations detected over the same time period for other herbicides. There was no apparent temporal trend in dissolved pendimethalin concentrations for all treatments.

The study demonstrates that herbicide transport by runoff mainly depends on the time to runoff and the runoff rates. The percentage herbicide losses were <1% for all compounds irrespective of their chemico-physical properties. It is important to note that the study was a small-scale experiment and that runoff dynamics may change on a field-scale.

ACKNOWLEDGEMENTS

We thank Don McNaughton, Hort Research, Ruakura for technical help with the HPLC analyses. This study was supported by a Post Doctoral Fellowship from AgResearch.

REFERENCES


