# Summary

Six herbicides (atrazine, diuron, oxadiazon, glyphosate, oryzalin, isoxaben), selected to represent a range of physico-chemical properties and application rates, were applied to the kerb edge of a section of asphalt road. A weir fitted with automatic sampling equipment was used to sample runoff from the outlet of a gully pot drain until 25 mm rain had fallen. In order to avoid possible saturation of adsorption sites, the six compounds were applied in two groups on separate occasions. Atrazine was included in both application groups so that the effect of the different application dates could be seen. Although rain fell within a few hours of application on both of the application days, the amount was only sufficient to trigger drain flow sampling on one occasion. As a result there was a large difference in the lag time between application and drain flow sampling for the two application groups.

There were marked differences in both the patterns of wash-off and the overall percentage losses between the two groups of compounds. For the three compounds that were applied when drain flow sampling was triggered on the day of application, all were detected in the first drain flow to be sampled after application and overall losses ranged from 38% of applied glyphosate to77% of applied atrazine. For this group, concentrations of herbicides peaked soon after drain flow began and then decreased rapidly. The first 5 mm of rainfall caused the majority of the measured wash-off and overall losses were almost complete after 13 mm of rainfall. Small amounts of glyphosate continued to be washed off the road surface until the end of the study. It is possible that this was also the case with the other two compounds, but analytical levels of quantification were not small enough to confirm it. For the four compounds applied on the second occasion when sampling was not triggered until 10 days after application, only three (atrazine, oryzalin and oxadiazon) were detected in drain flow at concentrations above their level of quantification, their overall losses ranging from 4% of applied oryzalin to20% of applied atrazine. Isoxaben was not detected in any samples of drain flow but was detected in gully pot sediment, indicating that it had been washed off the road surface. Concentrations of detected compounds again peaked soon after drain flow sampling was triggered, but decreased more slowly than after the first application. The majority of measured wash-off occurred after 7 mm of rainfall and total losses were complete after 12.8 mm of rain. The differences between the two application groups suggest that environmental factors such as time delay to rainfall and the detailed pattern of rainfall following application may be critical factors in determining wash-off.

Multiple regression analysis confirmed that the time lag from herbicide application to initiation of drain flow sampling was the main factor affecting total herbicide losses whereas individual correlation analysis for each of the two treatments suggested that $K_{OC}$ and solubility could be important factors in determining relative differences in losses between compounds. The reasons why isoxaben was not detected in wash-off are unclear, but probably relate to a combination of its low application rate, its 10 day residence time on the road

surface or in the gully-pot before drain flow sampling was triggered and its susceptibility to photolysis and / or adsorption.

This pilot study has demonstrated the value of outdoor experiments for measurement of herbicide losses from non-agricultural surfaces under natural conditions. Further studies are needed to:

- Confirm the significance of any relationships between herbicide losses, physico-chemical properties and rainfall patterns.
- Investigate losses from different types of surfaces such as railway track-beds.
- Investigate losses at a larger catchment scale.

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Opinions expressed within this paper are those of the authors and do not necessarily reflect the opinion of the sponsoring organisations. No comment within this report should be taken as an endorsement or criticism of any herbicide compound or product.

# Internal auditor

C D Brown

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# 1 Introduction

Herbicides are commonly used for total weed control on non-agricultural surfaces such as footpaths, road edges and railway track beds. There has been concern over the extent to which such non-agricultural herbicides are detected in surface water resources in and around urban areas. However, there is limited understanding of the processes involved in the fate of herbicides used on ‘hard’ surfaces, and little information on the extent to which contamination of water has arisen from correct use of compounds.

A consortium of sponsors from government and industry funded a project to investigate the losses of herbicides from a variety of man-made surfaces to which they may be applied and to develop a first-step regulatory risk assessment for such situations. A review was carried out, identifying kerb edges of roads as one of the main areas where non-agricultural herbicides are used (Heather, 1997). The current UK guidelines for environmental exposure assessments of pesticides for use on land not intended to bear vegetation (Corcoran, 1996) assume 100% of the applied compound is washed off the surface to drains in the first 25 mm of rainfall after application, but there were few data to support this assumption.

In order to gather preliminary data, a ‘pilot study’ was carried out to investigate the extent to which herbicides were washed off a kerb edge and drainage channel alongside an asphalt trunk road (the A6) running through the village of Shardlow, Derbyshire. The study aimed to characterise drain flow in response to rainfall and to quantify the movement of the herbicides from the place of application into the drainage system. The main objectives of the study were to:

1. Determine the extent to which a range of herbicides are washed off a road edge during natural rainfall;

2. Establish the proportion of applied herbicide washed off the test surface at different stages in the drain flow hydrograph;

3. Observe processes influencing the fate of herbicide after application and during the wash-off process.

This report describes the materials, methodology and results of the study, discusses the results in terms of the percentage losses of each herbicide and makes recommendations for further studies to be carried out within the wider consortium project.

# 2 Materials and methods

## 2.1 Selection of study site

The study site consisted of 16 m of asphalt road with concrete kerb stones and a grass verge on the A6, 200 m south of the Cavendish bridge at Shardlow, Derby. The road was drained through iron grilles to gully pots which then discharged onto the grass sides of the road embankment. Each gully pot had its own drain and discharge, rather than feeding a longitudinal sewer as is sometimes the case. The site was part of a longer section of similarly drained road and was chosen because the drains did not discharge into a ditch or other water course thus ensuring that any residues washed off would not affect aquatic flora and fauna.

The length of the site was determined by the spacing between the drain grilles. This was identified by pouring clean water onto the road and observing the direction of flow in order to define the catchment boundaries for the drain. The road was on a slight incline and, when the false fall was included, the catchment ran for the full 7 m width of the road, from 15 m to the north of the grille to 1 m south of it (Figure 1). Thus the catchment area was 112 $m^2$. The site was chosen in consultation with local Environment Agency staff and Leicestershire County Council Highways Department.

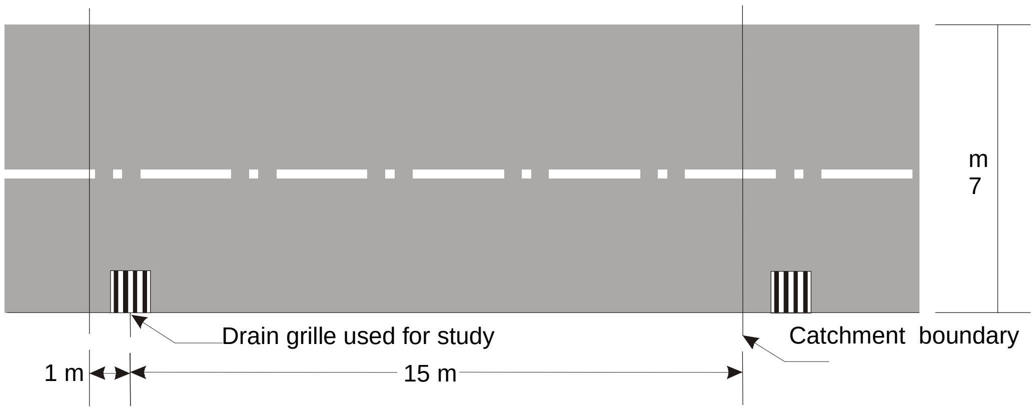



**Figure 1**: Layout of the study site

Prior to the first herbicide application, stones and debris were removed from the road gutter which was then swept using a yard brush. This was not normal practice but was necessary to remove an accumulation of dirt resulting from road construction work nearby (see Plate 1) and to avoid the need for the road to be swept by the County Council.

**Plate 1**: View of the road where the study was carried out, looking north showing debris in the gutter

## 2.2 Selection of test compounds

Six test compounds were nominated by the project steering group to provide a broad range of physico-chemical properties and herbicide application rates. Details of the compounds chosen and their physico-chemical properties are listed in Table 1 and Table 2. Experimental permits were obtained for those compounds not currently registered for non-agricultural use.

**Table 1**: Test compounds selected for the study

| Compound | Product | MAFF number | Formulation $g.L^{-1}$ AS; type | Application rate $L.ha^{-1}$ product | Application rate $g.ha^{-1}$ AS |
|---|---|---|---|---|---|
| Glyphosate | Roundup Pro Biactive | 04146 | 360; SL | 5.0 | 1800 |
| Diuron | Freeway | 06047 | 500; SC | 5.4 | 2700 |
| Atrazine | MSS Atrazine 50 FL | 01398 | 500; SC | 6.0 | 3000 |
| Oxadiazon | EXP30680B | - | 300 [1]; WP | 15.0 [1] | 4500 |
| Oryzalin | Surflan | - | 480; SC | 3.6 | 1728 |
| Isoxaben | Flexidor | 05104 | 125; SC | 0.6 | 75 |

Key to formulation types:
AS: Active substance, SL: Soluble concentrate, SC: Suspension concentrate, WP: Wettable powder
[1] Oxadiazon is formulated as a wettable powder at 300 g $kg^{-1}$ and applied at a rate of 15 kg $ha^{-1}$

**Table 2**: Physico-chemical properties of the test compounds

| Compound | $K_{OC}$ $mL.g^{-1}$ | Soil $DT_{50}$ Days | Solubility in water $mg.L^{-1}$ | Photolysis $DT_{50}$ |
|---|---|---|---|---|
| Atrazine | 100 | 35 - 50 | 33 | - |
| Diuron | 480 | 90 - 180 | 36.4 | - |
| Glyphosate | 10000* | 47 | 11600 | - |
| Oxadiazon | 3200 | 60 | 1 | - |
| Oryzalin | 700 - 1100 | 63 | 2.6 | Aqueous 1.4h |
| Isoxaben | 1400 | 90 - 120 | 1.42 | Susceptible to aqueous photolysis |

Data supplied by individual herbicide manufacturers
*Lower quartile value. The $K_{OC}$ of glyphosate has been measured at between 886 and 60000 for a range of soils

## 2.3 Application of test compounds

Herbicide application was split into two groups applied on separate occasions, with atrazine being included in each group (Table 3). There was concern that there might be insufficient adsorption sites for the compounds to be retained on the road surface if all six compounds were applied simultaneously.

The first group was applied on 14 October 1997 and the second on 01 December 1997, this second application being relatively late in the season. Nevertheless air temperatures were similar to those experienced during spring applications. A ‘Metfax’ weather forecast was obtained to check that rainfall was not expected on the day of application. Despite this and checking weather forecasts on local radio, rain fell on both application days.

Atrazine was included in both groups so that the effect of the different application dates could be seen. The products were applied individually rather than as a tank mix, since the compatibility for mixing the formulations was not known.

**Table 3**: Application dates and quantities of active substance applied at each application

| Compound | Date of herbicide application | | Quantities applied | |
|---|---|---|---|---|
| | 14 October 1997 | 1 December 1997 | Active substance (g) | Water volume (L) |
| Glyphosate | ● | | 0.86 | 0.12 |
| Diuron | ● | | 1.30 | 0.22 |
| Atrazine | ● | ● | 1.44 | 0.12 |
| Oxadiazon | | ● | 2.16 | 0.12 |
| Oryzalin | | ● | 0.83 | 0.12 |
| Isoxaben | | ● | 0.04 | 0.12 |

A ‘Vermorel 2000 HP’ 20 L knapsack sprayer was fitted with a Lurmark 015E80 nozzle and calibrated prior to application. An advantage of the piston sprayer design was that it was better able to empty the tank than a diaphragm sprayer. This was important because only small quantities of spray mix were being applied (see Table 3) and any left in the tank could significantly reduce the amount applied.

The required amount of each product was weighed into a measuring cylinder and mixed with the appropriate amount of water for spraying. The spray solutions were placed in labelled bottles in a dark box for transport to the test site. About ten minutes were left between each spraying so that the road was dry before the next application. The spray line was cleaned out by spraying an equal quantity of clean water through the sprayer after the chemical had dried on the kerb edge. This was sprayed along the full length of the kerb at the same rate as the original spray mix to ensure that all the product was applied and to prepare the sprayer for the next application.

The spray was applied in a continuous swath approximately 0.3 m wide along the full length of the test site. Only the side of the road with a grass verge was sprayed. Recommended practice is to spray so that the grass at the edge of the verge is treated as well as the kerb stones, but to apply none to the gutter channel itself (NAAC and BAA, 1998). However, local practice was to spray along the kerb to kill encroaching weeds but to allow the spray swath to also treat the edge of the gutter, in order to prevent weed growth in the joint between the road and the kerb. In this study, the swath was aligned so that the top and side of the kerb stone and the joint of the kerb with the road gutter were treated. It was considered important to be able to quantify the amount applied to the 'hard' surfaces and hence the grass verge was not treated.

Drain grilles were covered with black plastic bin liners during spraying so that none of the test compounds entered the gully pot directly. This was contrary to normal practice where the drains would be left uncovered and might be subject to over-spraying. For this study it was considered important to eliminate direct entry of herbicide to the drainage system, as this would have distorted analysis of wash-off from the road surface itself.

## 2.4 Sampling equipment and method

A miniature weir was used to measure flow from the drain outfall. A data logger was configured to begin monitoring the weir as soon as 0.2 mm of rain was detected in a tipping bucket raingauge installed at the site. The weir was monitored at 30 second intervals and the quantity of water flowing accumulated in the logger's memory. Once the first litre of water had passed, the logger triggered an automatic sampler to take 0.25 L of water from a chamber immediately downstream of the weir crest, subject to a float switch indicating that sufficient water was present.

After the first sample, the logger triggered the sampler when each additional 40 L of water had been discharged from the drain. The sampling interval was chosen so that the full 24 bottle capacity of the sampler would be used in a nominal 10 mm rainfall event, assuming that 1.5 mm rainfall was required to wet up the surface and there were no losses from the system:

i.e.: 7 m x 16 m = 112 $m^2$, giving 112 L per mm rainfall (with no losses).

Therefore a 10 mm rainfall event would yield: (10-1.5) x 112 = 952 L water.

So: 952 L / 40 L interval = 23.8 samples.

In practice the amount of rainfall required to wet up the surface and initiate flow varied depending upon the temperature of the surface and the intensity of the rainfall event; for example, on one occasion in early December, 0.8 mm of rain was sufficient to cause the drain to flow for a short time. The data logger was set so that monitoring of the weir would cease after six hours without rain. Air temperature at the site was recorded every two hours, regardless of rainfall.

A scheme of the weir box is given in Figure 2, showing the layout of the components. The drain entry to the weir chamber was below the water line to minimise disturbance of the water. The weir box is shown *in situ* in Plate 2, which shows the dual-chamber construction, allowing samples to be taken from a chamber downstream of the weir without interfering with the flow measurement. The float switch was fitted through the weir chamber wall so that all fittings were protected from accidental damage. The control logger, battery, weir box and auto-sampler were all housed in a wooden box below the drain outfall (Plate 3). The floor of the box was built using a wooden pallet so that water could drain away onto the embankment side after discharge from the weir box. The main items of equipment used are listed in Table 4.

The site was visited as soon as practicable after rainfall to collect the water samples. The auto-sampler was then re-stocked with clean bottles and flow data collected from the logger. If monitoring had ceased, then the logger memory was cleared and the program reset. Water samples were decanted into HDPE bottles and stored frozen or chilled as appropriate, ready for despatch to the analytical laboratories. Each sample was given a unique identifier and a record was kept showing the auto-sampler bottle from which it came. The glass bottles were then washed with acetone and oven dried ready for re-use.

Sampling continued until a total of 25 mm of rain had fallen, so that the data collected could be compared with the assumptions made in the PSD tier 1 model (Corcoran, 1996).

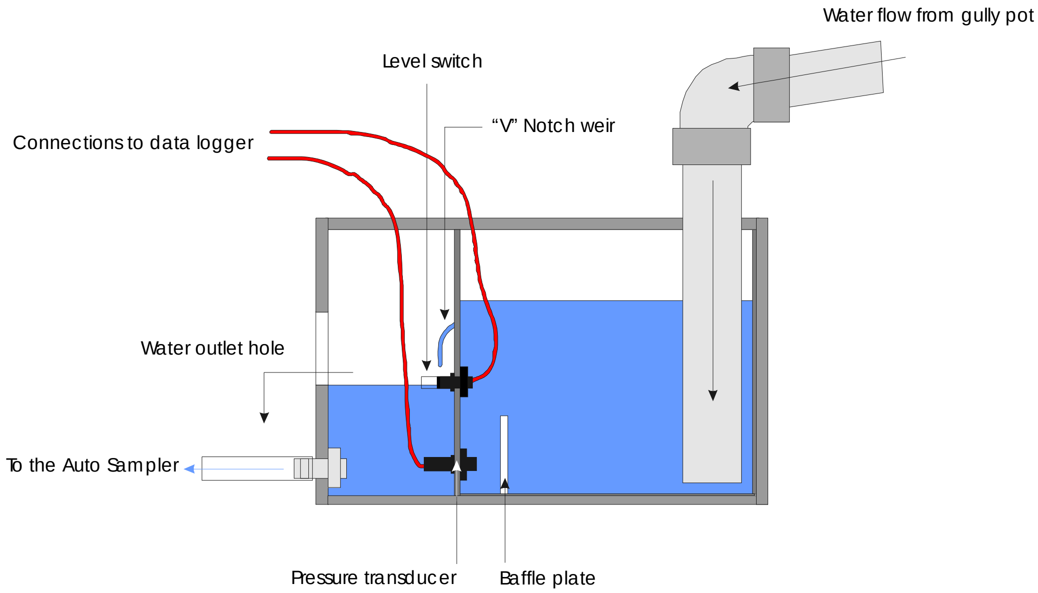



**Figure 2**: Schematic section through the weir box

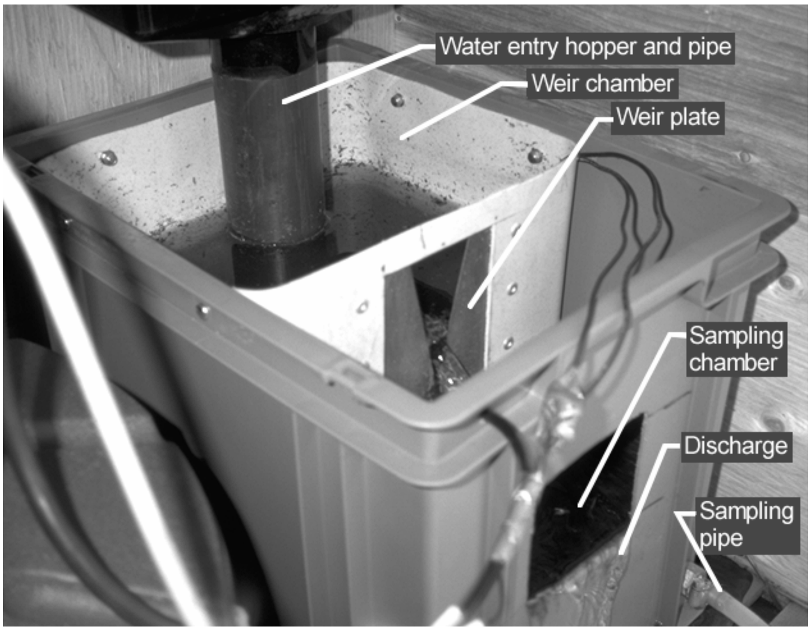



**Plate 2**: Weir box *in situ* with drain flowing

**Plate 3**: Overview of the monitoring installation

**Table 4**: Main items of field equipment used

| Function | Supplier and model |
|---|---|
| Control logger | Delta-T Devices DL3000 |
| Auto-sampler | Montec Epic 1010, 24 bottle carriage with glass ‘wedge’ bottles |
| Weir plate | Brass plate v-notch, 28 degrees x 100 mm high, fabricated & calibrated in-house |
| Weir depth sensor | Druck PDCR 810 series, 1 bar range, calibrated in-house |
| Rain gauge | Delta-T Devices RG1 tipping bucket, 0.2 mm per tip |
| Thermometer | Delta-T Devices AT1 shielded thermistor |

## 2.5 Control waters and sediment

A 1 L sample of water was taken from the drain prior to the first treatment, on 08 October 1997. Sub-samples were analysed for traces of all the applied compounds although the County Council had advised that glyphosate was the only compound used to treat roads in the area of the experiment.

A further 1 L sample of water was taken from the drain and dried to determine the dry matter content.

Sediment from the gully pot was also taken and analysed for physical and chemical composition in SSLRC's soil physics laboratory.

## 2.6 Analysis

Drain water samples were sent to analytical laboratories packed in insulated containers with ice packs to keep them frozen and thus minimise degradation of any residues present. Different laboratories were used for different groups of compounds (Table 5) depending upon sponsorship and analytical capability. Herbicide concentrations were determined by documented methods developed by the individual analytical laboratories.

**Table 5**: Analytical laboratories used and limits of detection

| Compound | Laboratory | Lower Validation Limit (LVL) $\mu g.L^{-1}$ |
|---|---|---|
| Glyphosate | Institut Fresenius, Hamburg D | 0.05 |
| Diuron | Rhône-Poulenc, Ongar UK | 100 |
| Atrazine | Rhône-Poulenc, Ongar UK | 100 |
| Oxadiazon | Rhône-Poulenc, Ongar UK | 100 |
| Oryzalin | Dow AgroSciences, Wantage UK | 50 |
| Isoxaben | Dow AgroSciences, Wantage UK | 50 |

The relatively high LVLs given for most compounds in Table 5 were considered acceptable for this study where it was anticipated that there would be relatively little attenuation of applied compounds both before and during wash-off. Nevertheless, in some cases the analytical laboratories also estimated concentrations between the LVL and 20 % of the LVL.

# 3 Results

## 3.1 Rainfall and air temperature

Daily rainfall during the two study periods is shown in Figure 3 and Figure 4. It can be seen that there was some rainfall on the spray day of both treatments.

The first application of herbicides (14 October 1997) was made in the morning and rain started to fall within six hours. This was a sufficiently large event (3 mm) to cause drain flow and sampling during the first day after application. There was then a relatively dry period lasting until early November, when a succession of heavy showers led to more drain flow and sampling. The 25 mm target rainfall fell by 08 November - 25 days after application.

Rain also fell on the spray day of the second treatment, but only amounted to 0.8 mm. Due to a change in the behaviour of the weir (discussed in section3.2) this was insufficient to trigger the sampler, although approximately 7 L was discharged through the drain over a period of two hours. No further rain fell until 9 days after spraying, when 0.6 mm fell, with a further 6.4 mm falling over the next two days. The 25 mm target rainfall fell within 23 days of application.

Air temperature for each treatment is shown in Figure 4. It can be seen that the diurnal range was greater during the middle period of the first treatment, with air frosts at night. This led to heavy dews which were dried out by direct sunlight in the mornings. The rainy period at the end of October was relatively warm with little night-time drop in temperature.

The second treatment was characterised by more frontal activity and thus a lower diurnal range and less frost. There was also less direct sunlight on the study area. The mean temperature for the 28 days after application was a little lower for the second treatment than the first (5.8ºC compared to 7.8ºC after the first treatment).

## 3.2 Drain Flow

After installation, the brass weir plate soon tarnished and this led to a reduction in the height of the meniscus that could be retained by the weir. This in turn led to a change in the calibration of the weir, which was not corrected until after the study. The depth measurements taken by the logger were retained in addition to the calculated flow and so it was possible to recalculate the flow based upon the new weir calibration once the study was complete. This source of error meant that the samples were taken at greater intervals than originally planned and highlighted the sensitivity of such a small weir to relatively small changes in the sensors. The flow data should be considered estimates rather than accurate measurements.

Drain flow after the two treatments is shown at hourly intervals in Figure 3 and Figure 4. The hydrographs show clearly how the drain responds to rainfall, with both a steep increase and decrease in flow. Events were often complete within two hours. The hydrographs demonstrate that no water moved between rainfall events, unlike a river where there is usually a base flow.

Rainfall on the day of the first treatment caused a peak flow of over 100 L.hr$^{-1}$ , followed by greater drain flow on the following day. A smaller, separate flow event followed on the third day. There was then a 19 day period of no drain flow until early November when the rainfall described above caused two flow peaks during the night of 04-05 November. There were then two wet days with large flow at the end of the study.

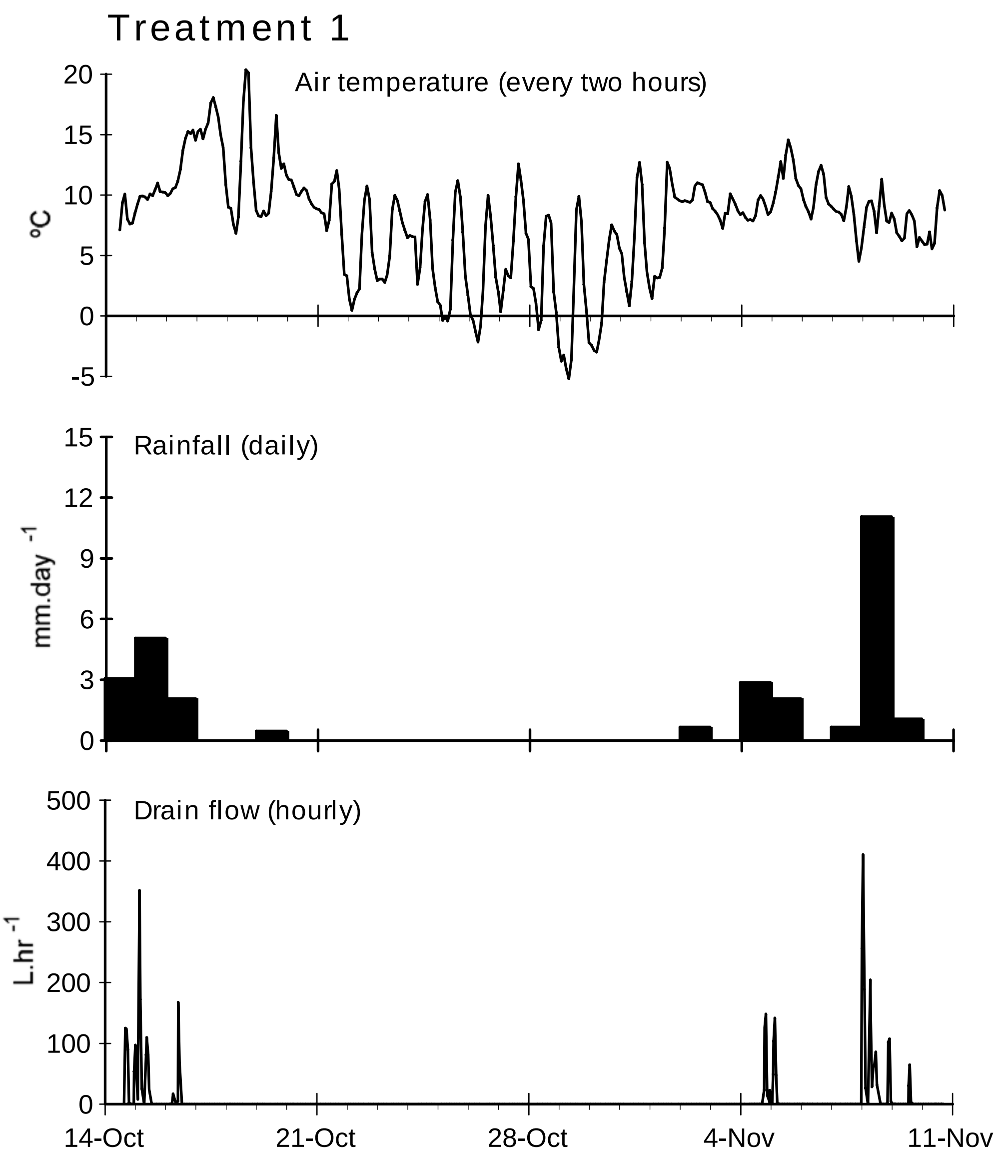



**Figure 3**: Air temperature, rainfall and drain flow after the first treatment

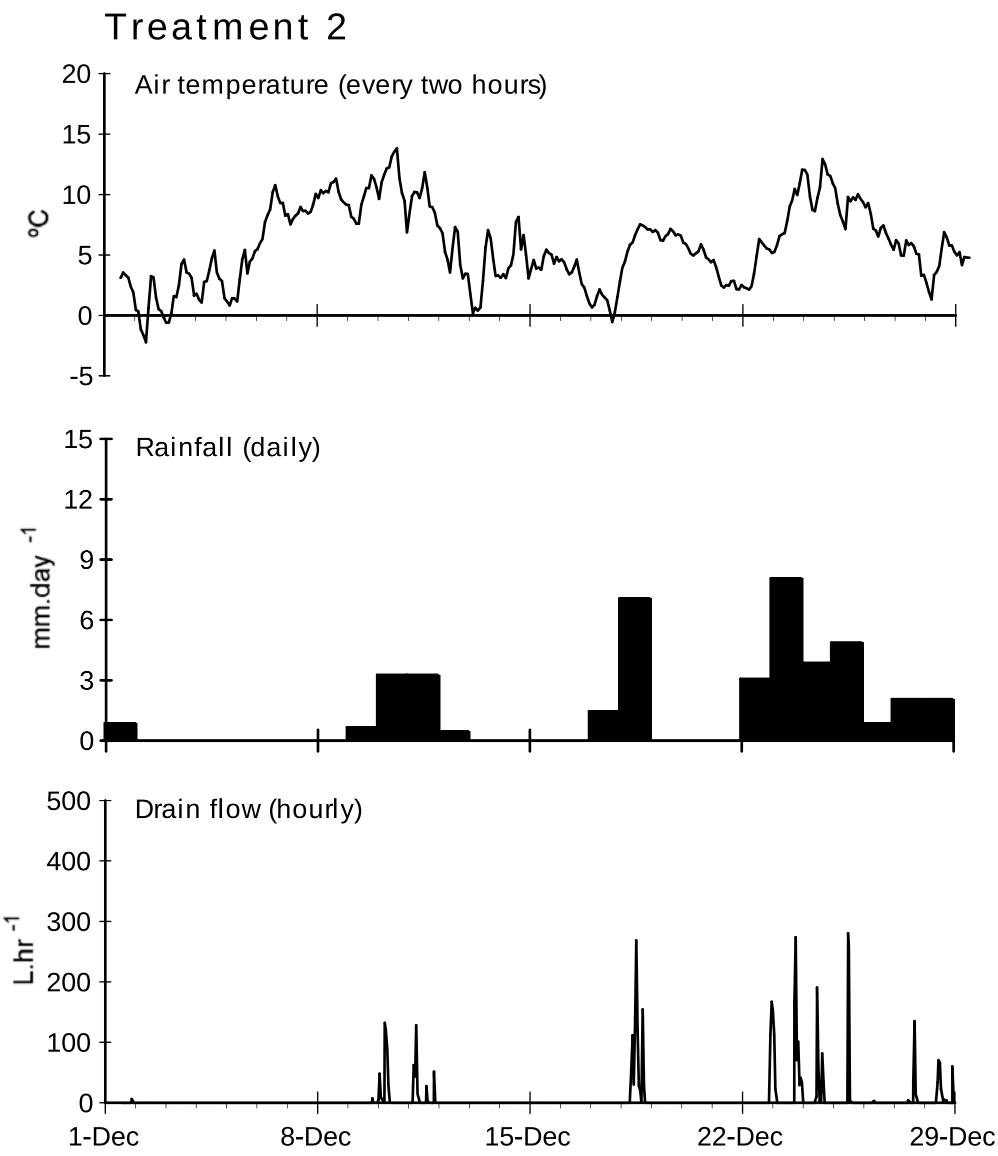



**Figure 4**: Air temperature, rainfall and drain flow after the second treatment

The effect of the rainfall on the day of the second treatment can just be seen as a small mark on the hydrograph during the night of 01-02 December. There was then no flow until late on the ninth day after application when another small mark on the hydrograph indicates minor drain flow in response to the small amount of rain that fell. Significant amounts of rain on the two subsequent days initiated sampling, with drain flow of up to 100 $L.hr^{-1}$. The second treatment was then characterised by more events yielding flow at around 200 $L.hr^{-1}$ with no more than five consecutive dry days.

A more detailed example of the hydrograph for a single event is given in Figure 5 which shows the flow from the drain at one minute intervals. The drain began to flow after the fifth tip of the rain gauge (*i.e.* after 1 mm rain) and the rate flow increased quickly over about three minutes. Flow increased again in response to more intense rain but fell when the rainfall intensity fell. The drain stopped flowing within about 30 minutes of rain stopping.

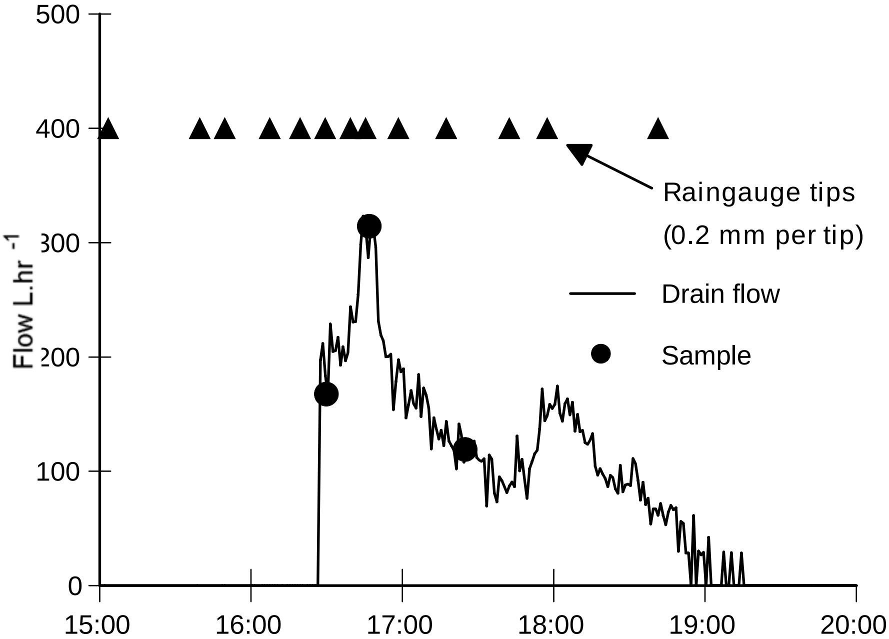



**Figure 5**: Drain flow hydrograph for 14 October 1997

## 3.3 Herbicide concentrations

### 3.3.1 In control water and sediment

The 1 L drain water sample was found to contain 300 mg.L$^{-1}$ dry matter. Glyphosate was detected in the control water at a concentration of 11 µg.L$^{-1}$. None of the other five compounds were detected in the control water. Glyphosate was the only compound known to have been previously used within the catchment (see section 2.5, p. 8) although the date of its latest application was not known. Its presence in the control waters suggests either its recent usage, or that compounds applied to hard surfaces may remain available for export via drainage waters for considerable periods after application.

The drain sediment composition is shown in Table 6.

Filtrate representing suspended sediment from water samples taken during the second treatment was found to contain 139 µg.kg$^{-1}$ isoxaben and 302 µg.kg$^{-1}$ oryzalin.

**Table 6**: Gully pot sediment physical and chemical properties

| Particle size distribution (peroxidised, oven-dry) | |
|---|---|
| 600 µm - 2 mm | 23.31 % |
| 212 µm - 600 µm | 38.50 % |
| 106 µm - 212 µm | 12.07 % |
| 63 µm - 106 µm | 4.10 % |
| 2 µm - 63 µm | 9.01 % |
| | |
| Chemical properties (air-dry) | |
| pH (1:5 in water) | 8.1 |
| pH (1:5 in KCl) | 7.9 |
| CEC | 4.2 mEq.100 $g^{-1}$ |
| Organic carbon | 3.4 % |

### 3.3.2 In drain flow

Herbicide concentrations over time are shown for each treatment in Figure 6 and Figure 8. Details are given in the Appendix (8.2.1 and 8.2.2).

All three compounds (atrazine, diuron, glyphosate) in the first treatment were detected in the first drain flow event, with the concentration increasing to a peak value within about 15 minutes . There was then a decrease in concentration over a period of approximately 9 hours as the drain continued to flow. At the end of this period and during subsequent sampling events over the next 30 hours, concentrations were an order of magnitude smaller than peak values. Further sampling on 04, 05 and 08 November showed relatively small and decreasing concentrations of all three compounds, though quantification for atrazine and diuron is uncertain because levels were below the lower validation limit.

Concentrations from the second treatment (Figure 7) were generally smaller than from the first. Isoxaben was not detected in any of the samples, but its presence in the gully pot sediment showed that it had been washed off the road surface. It should be noted that, if all 646 litres of drain flow resulting from the 7 mm of rain that fell during the first two days of sampling (10 and 11 December) contained isoxaben at an average concentration of 5 µg.$L^{-1}$ it would represent 8% of the applied amount.

The peak atrazine concentration in the second treatment was around 25% of that from the first. This maximum concentration was detected in the first sample collected whereas the maximum for oxadiazon was in the fourth sample taken six hours after the first. Following these peaks, the rate of decline in concentrations over time was slower than that observed after the first treatment. Atrazine concentrations were only reduced by one order of magnitude after approximately 33 hours. The pattern of concentrations for oryzalin is complex, probably because all determinations are at or below the lower validation limit. Following the initial sampling event, there was no further sampling until significant rainfall triggered drain flow several days later. As with the first treatment, traces of the applied compounds were detected, but at levels below the lower validation limit.

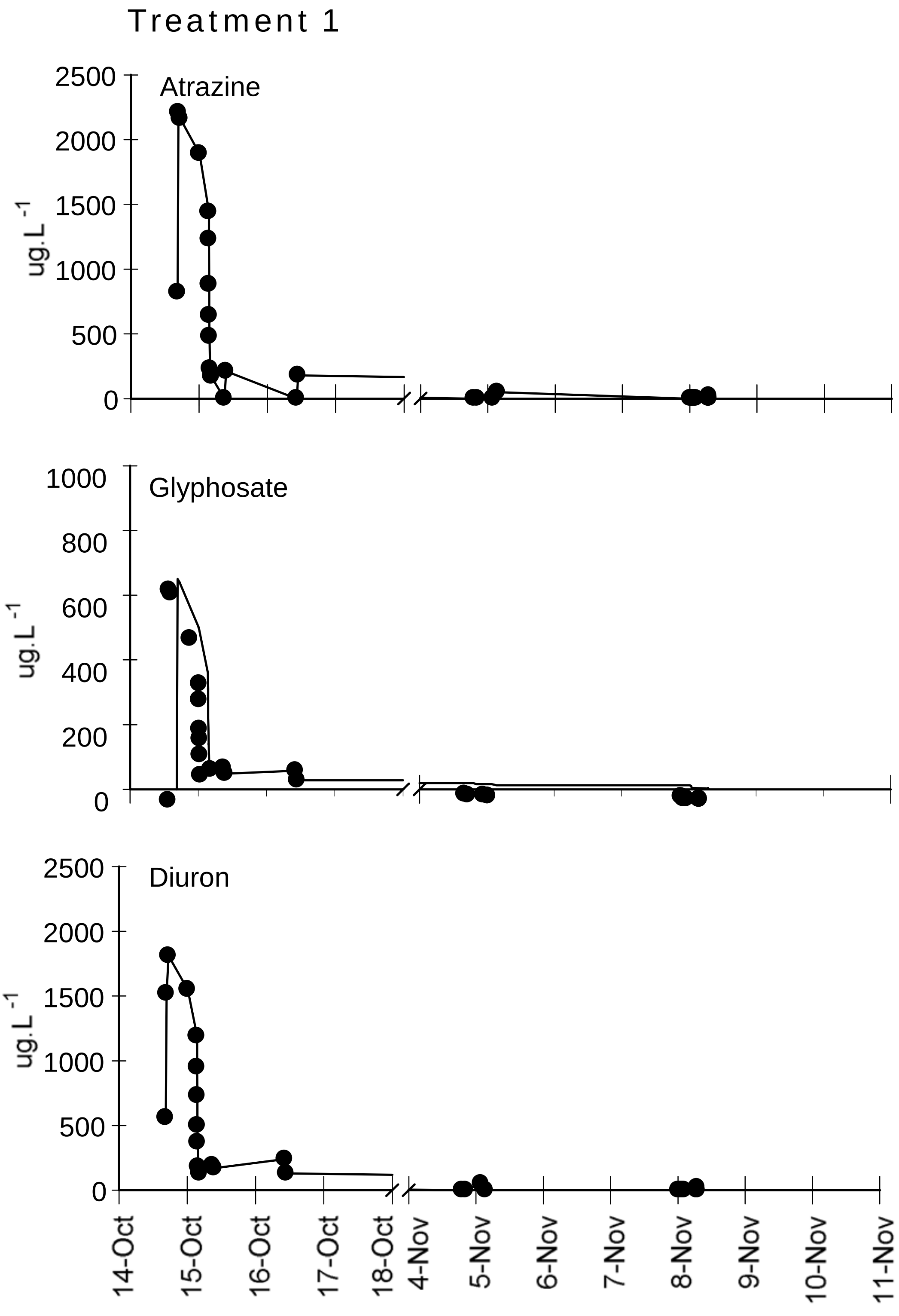



**Figure 6**: Herbicide concentrations in drain water after the first treatment

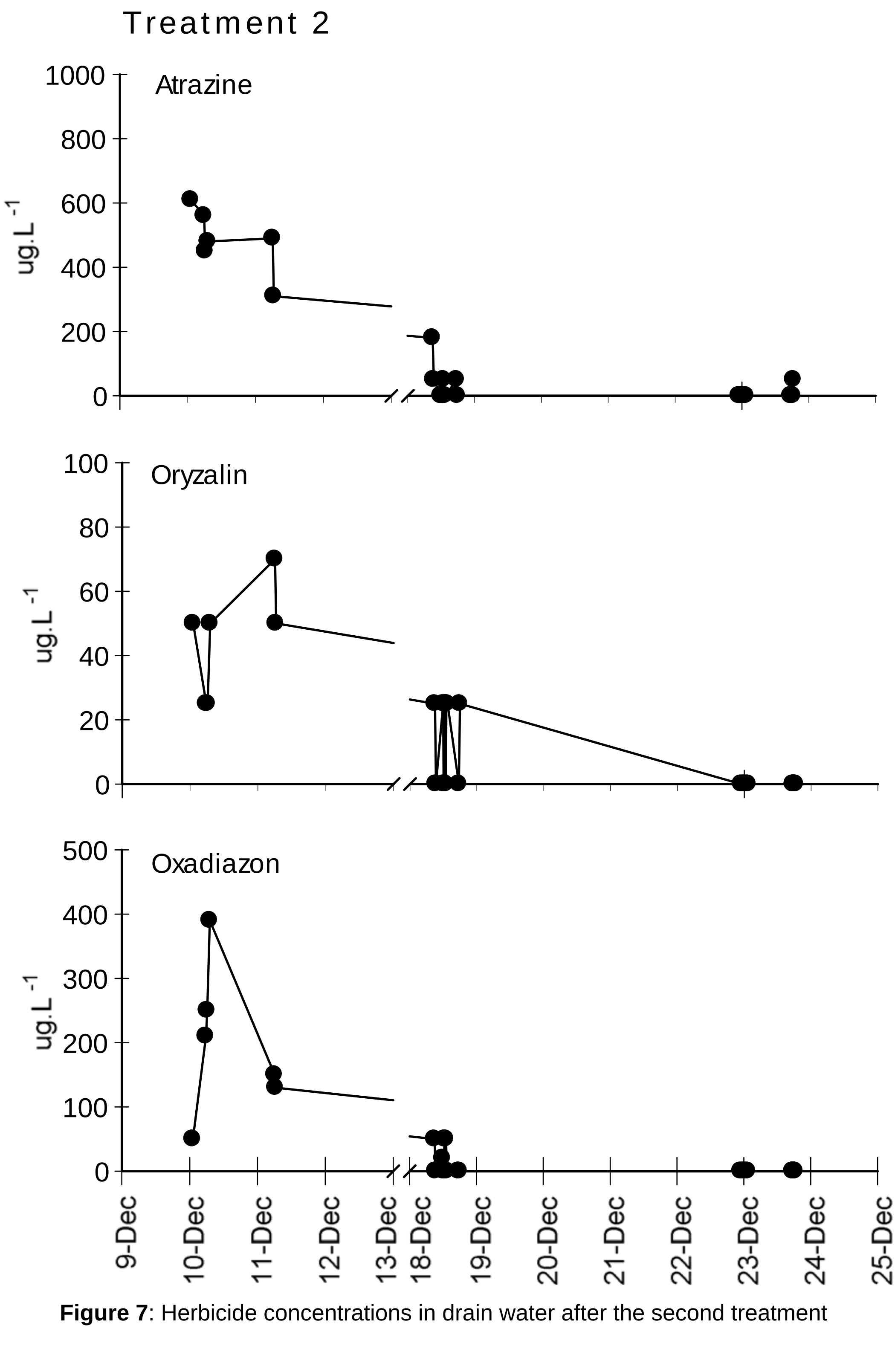
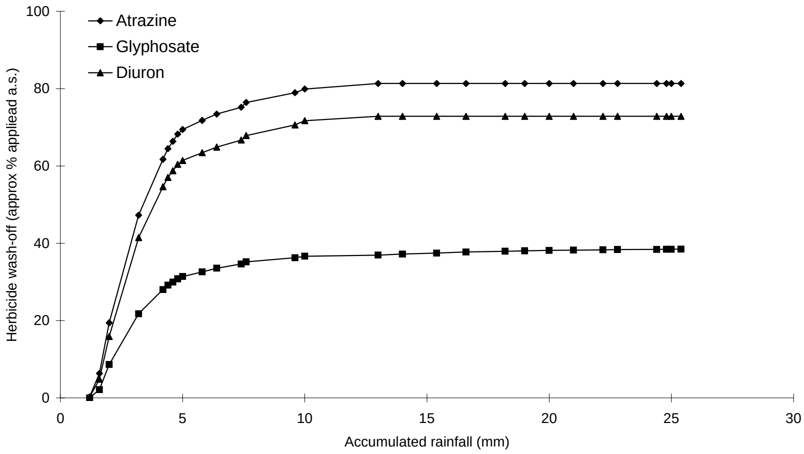



**Figure 7**: Herbicide concentrations in drain water after the second treatment

## 3.4 Proportional wash-off

Accumulated wash-off of the six compounds was calculated and is shown in Figure 8, plotted against accumulated rainfall. No results are given for isoxaben because its relatively large limit of detection compared to its small application rate means that percentage losses cannot be calculated with any confidence. It should also be noted that flow data are an estimate from the weir depth measurements and so the proportional wash-off is approximate. The charts should be used for comparison only. The total wash-off by the end of the experiment (25 mm rainfall) is given in Table 7.

### Treatment 1




### Treatment 2

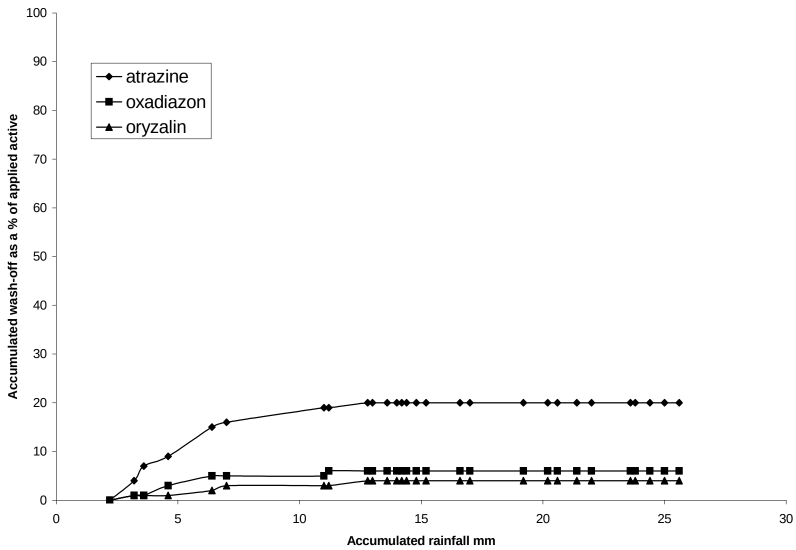



**Figure 8**: Proportional wash-off with accumulated rainfall

**Table 7**: Accumulated wash-off after 25 mm rainfall

| Compound | Approximate proportion lost after 25 mm rainfall (% of applied active substance) | |
|---|---|---|
| | Treatment 1 | Treatment 2 |
| Glyphosate | 38 | |
| Diuron | 72 | |
| Atrazine | 77 | 20 |
| Oryzalin | | 4 |
| Oxadiazon | | 6 |

The first treatment showed the greatest wash-off, with the majority occurring within the first 5 mm of rainfall. Total accumulated losses were almost complete (94 to 98% of maximum loss) after about 8 mm of rain and for atrazine and diuron appeared to be complete after 13 mm of rain. However, small but detectable amounts of glyphosate continued to be washed off until the end of the study. The limit of quantification of atrazine and diuron was an order of magnitude greater than that of glyphosate, and it is thus possible that small non-quantifiable amounts of both atrazine and diuron also continued to be washed off until the end of the study.

For the second treatment, overall losses were significantly smaller, the accumulated loss of atrazine being less than one third of that from the first treatment. The majority of wash-off of all detected compounds occurred after 7 mm of rainfall and accumulated losses were complete after 12.8 mm of rain.

Atrazine showed the greatest total losses for both treatments. Relative losses of the other detected compounds in relation to atrazine were in the order of:

diuron > glyphosate > oxadiazon > oryzalin.

# 4 Data analysis and discussion

## 4.1 Relationships between wash-off and physico-chemical properties

The proportion of active substance (AS) lost by the end of each test was compared with $K_{OC}$, $DT_{50}$, and water solubility of the compounds to check for any possible relationships between physico-chemical properties and wash-off (Figure 9). No results are given for isoxaben because of its uncertain percentage losses (see section 3.4).

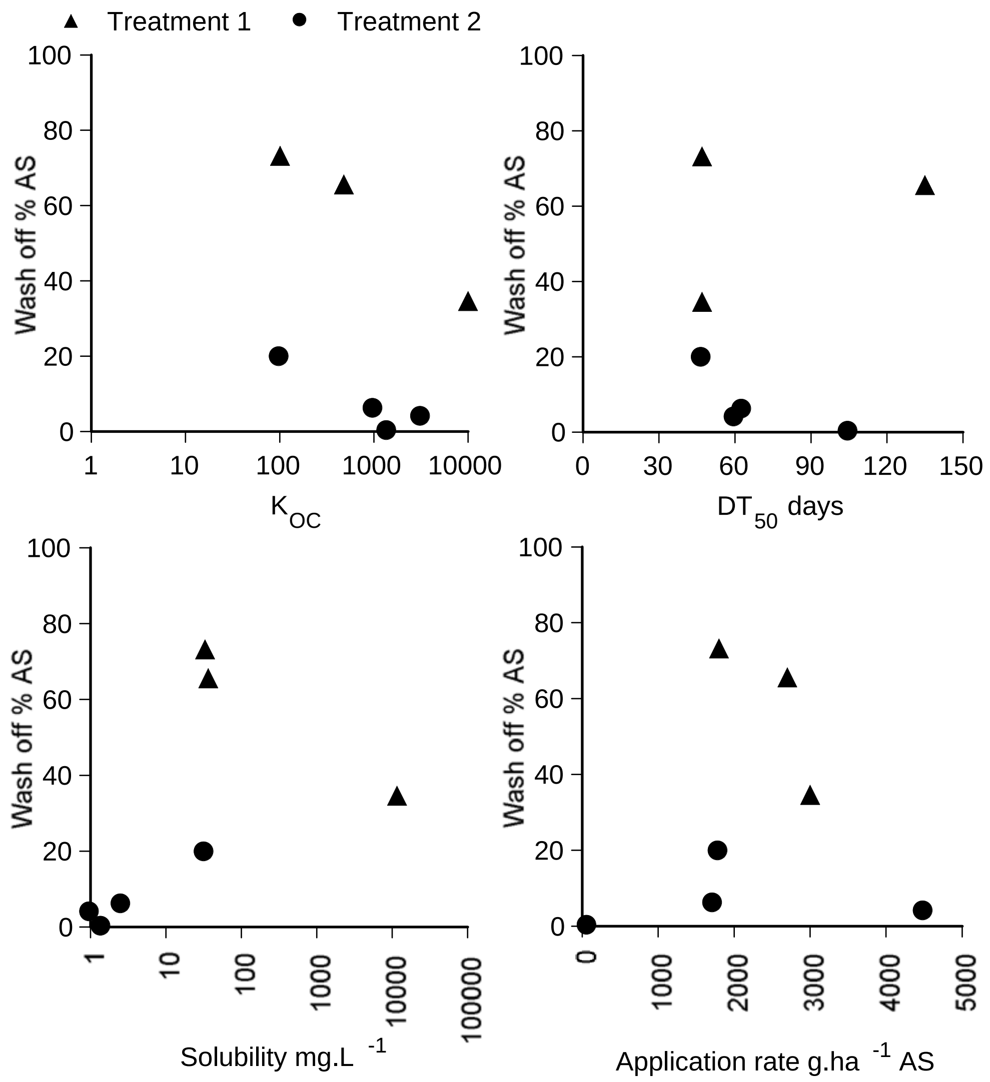



**Figure 9:** Wash-off versus $K_{OC}$, $DT_{50}$, Solubility and application rate of the compounds tested in both treatments

It is clear from Figure 9 that there are large differences between the two treatments. In order to try and take this into account, a multiple linear regression analysis was carried out with total percentage loss as the dependent variable and $K_{OC}$, solubility, $DT_{50}$, application rate and time from application to initial drain-flow sampling (lag time) as the independent variables. Other environmental factors such as mean air temperature and rainfall intensity also varied between the two treatments. However, because of the small number of data points available for analysis it was only possible to include a single environmental variable and lag time was considered to be the most important factor that differed between the two treatments. The small number of data points available for analysis means that the results should be treated with caution.

Only lag time, $K_{OC}$ and solubility showed any significant relationships with total losses. Results of multiple regression analyses involving two or more of these parameters are shown in Table 8.

**Table 8:** Multiple linear regression analyses of the factors influencing herbicide losses

| Independent variables | Adjusted $r^2$ | Relationship with total % losses | Significance [1] |
|---|---|---|---|
| Lag time, | 0.9608 | negative | * |
| $K_{OC}$, | | negative | n.s. |
| solubility | | positive | n.s. |
| Lag time, | 0.9722 | negative | **** |
| $K_{OC}$ | | negative | ** |
| Lag time, | 0.9333 | negative | *** |
| solubility | | negative | * |
| $K_{OC}$, | -0.0421 | negative | n.s. |
| solubility | | positive | n.s. |

[1] n.s. not significant, * significant at 95% CL, ** significant at 99% CL, *** significant at 99.5% CL, **** significant at 99.9% CL

Lag time was by far the most significant variable determining total losses. $K_{OC}$ and solubility were significant factors only for those regressions involving two variables, of which lag time was the first. However, in the regression where solubility was a significant variable, it was negatively correlated with total losses the opposite relationship to that expected. The results shown in Figure 9 indicate that this negative relationship resulted from the very large solubility of glyphosate compared to the other compounds in the first treatment and its relatively small measured losses compared to those of the other compounds. The $K_{OC}$ of glyphosate is also much larger than that of other compounds in the first treatment and it is thus likely that there are strong auto-correlations between solubility and $K_{OC}$ for this treatment. Confirmation of the influence of $K_{OC}$ and solubility on total losses would require a more controlled and replicated study where wash-off of all six compounds was compared under identical environmental conditions.

## 4.2 Implications of the results for the dissipation of herbicides applied to hard surfaces

The fact that an increased lag time between herbicide application and initiation of drain flow resulted in significantly reduced total percentage losses of compounds, indicates that they are being dissipated within the catchment. Possible mechanisms include degradation, immobilisation and physical removal.

The lack of any correlation between total losses and soil $DT_{50}$ for the compounds suggests that microbial degradation is not a significant factor. However, both oryzalin and isoxaben are susceptible to aqueous photolysis and this could contribute to their dissipation, especially if the small amount of rain that fell on their application day was sufficient to maintain a significant amount in solution for a significant period of time.

The significant negative correlations between observed total percentage losses and $K_{OC}$ suggest that significant amounts of the applied herbicides are adsorbed and retained within the catchment. Analysis of the gully pot sediment after the end of the second treatment confirmed that the applied compounds were present in this compartment, although the amounts represent only a very small fraction of the total applied. It is thus likely that adsorption and retention processes within the catchment, together with adsorption to gully pot sediment that is not removed in drainage waters represent important dissipation mechanisms in the hard surface environment.

No measurements were made to confirm whether there was any physical removal of herbicides from the catchment. However, observations made during visits to the site suggest a possible removal mechanism related to traffic movement. During some of the main rainfall events, heavy traffic was seen to be moving surface water along the road, both into and out of the catchment. It was also noted that spray from the wheels of vehicles was thrown from the road onto the adjacent grass verge. Both processes could have removed some of the applied herbicides from the study catchment and may thus account for some of the apparent dissipation that was indicated by the observed total losses.

# 5 Conclusions

Applying atrazine in both treatments showed how wash-off can vary under different environmental conditions. However, the different conditions for the two treatments reduced the confidence with which wash-off could be related to chemical properties.

The change in surface texture of the weir plate highlighted the difficulty of calibrating such small-scale equipment for field use although the retention of depth-sensor data allowed revised flows to be calculated retrospectively.

The following broad conclusions can be drawn from this pilot study:

- As little as 0.8 mm of rain could initiate herbicide wash-off from hard surfaces, whereas only 2 - 3 mm of rainfall was required to move significant amounts of herbicides out through roadside drains;

- The first 5 - 7 mm of rainfall after application were the most important and caused the most wash-off;

- For all detected compounds, accumulated wash-off was virtually complete after 13 mm of rainfall;

- Small amounts of glyphosate continued to be washed off the road surface until the end of the study. It is possible that this was also the case for all other applied compounds although the level of analytical quantification was too high to confirm it;

- The extent of wash-off appears to be dependent on the time delay from application to rainfall causing drain flow whereas relative losses of different compounds appear to be functions mainly of $K_{OC}$ and water solubility;

- With the exception of avoiding over-spray of drains, the environmental conditions of this study are likely to represent herbicide wash-off under worst-case conditions: strip application to a drained channel in a small catchment with no external dilution. Rainfall shortly after application could also be considered a realistic worst-case, causing drain flow within six hours of herbicide application.

# 6 Recommendations

This pilot study has demonstrated the value of outdoor experiments for measurement of herbicide losses from non-agricultural surfaces under natural conditions. It has identified a number of factors that may be important in determining the loss of herbicides from a specific type of man-made surface. However, limitations arising from the worst-case nature of the study and the limited data generated mean that further studies are needed to clarify a number of questions arising from the results and data analysis. It is therefore recommended that:

- Controlled wash-off studies should be undertaken to investigate the relationship between time delay to rainfall, volume of rainfall, physico-chemical properties and percentage losses. A variety of surfaces should be included.

- A further study should be carried out to gather data representative of herbicide wash-off from railway track-bed formations, the other major man-made surface to which herbicides are applied.

- Attempts should be made to gather data from a larger catchment with only a proportion of sealed surfaces, some of which are untreated, in order to get an idea of the potential impacts of dilution as a result of run-off from untreated areas.

# 7 References

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Parsons R G, Brockelsby C D and Newby S (1998): Adherence of herbicides to hard surfaces: In: Proceedings 9th international congress on pesticide chemistry - the food-environment challenge. Held at Westminster, London, August 1998. Page 6C-02.

# 8 Appendix: data tables

## 8.1 Daily rainfall

| First treatment | | Second treatment | |
|---|---|---|---|
| Date | Rainfall mm | Date | Rainfall mm |
| 14 Oct | 3 | 01 Dec | 0.8 |
| 15 Oct | 5 | 02 Dec | - |
| 16 Oct | 2 | 03 Dec | - |
| 17 Oct | - | 04 Dec | - |
| 18 Oct | - | 05 Dec | - |
| 19 Oct | 0.4 | 06 Dec | - |
| 20 Oct | - | 07 Dec | - |
| 21 Oct | - | 08 Dec | - |
| 22 Oct | - | 09 Dec | 0.6 |
| 23 Oct | - | 10 Dec | 3.2 |
| 24 Oct | - | 11 Dec | 3.2 |
| 25 Oct | - | 12 Dec | 0.4 |
| 26 Oct | - | 13 Dec | - |
| 27 Oct | - | 14 Dec | - |
| 28 Oct | - | 15 Dec | - |
| 29 Oct | - | 16 Dec | - |
| 30 Oct | - | 17 Dec | 1.4 |
| 31 Oct | - | 18 Dec | 7 |
| 01 Nov | - | 19 Dec | - |
| 02 Nov | 0.6 | 20 Dec | - |
| 03 Nov | - | 21 Dec | - |
| 04 Nov | 2.8 | 22 Dec | 3 |
| 05 Nov | 2 | 23 Dec | 8 |
| 06 Nov | - | 24 Dec | 3.8 |
| 07 Nov | 0.6 | 25 Dec | 4.8 |
| 08 Nov | 11 | 26 Dec | 0.8 |
| 09 Nov | 1 | 27 Dec | 2 |
| 10 Nov | - | 28 Dec | 2 |
| 11 Nov | 0.6 | 29 Dec | 0.2 |
| 12 Nov | - | 30 Dec | - |

## 8.2 Analytical results

### 8.2.1 Herbicide concentrations in drain water: treatment 1

| Date and time | Atrazine µg.L-1 | Glyphosate µg.L-1 | Diuron µg.L-1 |
|---|---|---|---|
| 14 Oct 1997 16:30 | 820 | <20 | 560 |
| 14 Oct 1997 16:47 | 2210 | 650 | 1520 |
| 14 Oct 1997 17:25 | 2160 | 640 | 1810 |
| 15 Oct 1997 00:11 | 1890 | 500 | 1550 |
| 15 Oct 1997 03:27 | 1440 | 360 | 1190 |
| 15 Oct 1997 03:30 | 1230 | 310 | 950 |
| 15 Oct 1997 03:34 | 880 | 220 | 730 |
| 15 Oct 1997 03:38 | 640 | 190 | 500 |
| 15 Oct 1997 03:42 | 480 | 140 | 370 |
| 15 Oct 1997 03:54 | 230 | 77 | 180 |
| 15 Oct 1997 04:24 | 170 | 61 | 130 |
| 15 Oct 1997 08:54 | <20 | 66 | 190 |
| 15 Oct 1997 09:30 | 210 | 48 | 170 |
| 16 Oct 1997 10:19 | <20 | 57 | 240 |
| 16 Oct 1997 10:50 | 180 | 28 | 130 |
| 04 Nov 1997 19:07 | <20 | 19 | <20 |
| 04 Nov 1997 20:16 | <20 | 16 | <20 |
| 05 Nov 1997 01:50 | <20 | 16 | **50** |
| 05 Nov 1997 03:28 | **50** | 13 | <20 |
| 08 Nov 1997 00:16 | <20 | 12 | <20 |
| 08 Nov 1997 00:42 | <20 | 11 | <20 |
| 08 Nov 1997 01:04 | <20 | 5.1 | <20 |
| 08 Nov 1997 01:17 | <20 | 4.4 | <20 |
| 08 Nov 1997 01:54 | <20 | 4.3 | <20 |
| 08 Nov 1997 02:18 | <20 | 4.4 | <20 |
| 08 Nov 1997 06:50 | <20 | 2.6 | <20 |
| 08 Nov 1997 06:52 | <20 | 4.2 | <20 |
| 08 Nov 1997 06:54 | **20** | 3 | **20** |
| 08 Nov 1997 06:58 | <20 | 3.2 | <20 |

Numbers in bold indicate estimated values below the limit of quantification but above the limit of detection.
<20 - Below analytical limit of detection.

### 8.2.2 Herbicide concentrations in drain water: treatment 2

| Date and time | Atrazine µg.L$^{-1}$ | Oryzalin µg.L$^{-1}$ | Isoxaben µg.L$^{-1}$ | Oxadiazon µg.L$^{-1}$ |
|---|---|---|---|---|
| 10 Dec 1997 01:07 | 610 | 50 | <10 | **50** |
| 10 Dec 1997 05:46 | 560 | **25** | <10 | 210 |
| 10 Dec 1997 06:12 | 450 | **25** | <10 | 250 |
| 10 Dec 1997 07:08 | 480 | 50 | <10 | 390 |
| 11 Dec 1997 06:05 | 490 | 70 | <10 | 150 |
| 11 Dec 1997 06:24 | 310 | 50 | <10 | 130 |
| 18 Dec 1997 08:56 | 180 | **25** | <10 | **50** |
| 18 Dec 1997 09:18 | **50** | <10 | <10 | <20 |
| 18 Dec 1997 11:54 | <20 | **25** | <10 | **20** |
| 18 Dec 1997 12:03 | <20 | <10 | <10 | <20 |
| 18 Dec 1997 12:34 | <20 | <10 | <10 | **50** |
| 18 Dec 1997 12:43 | <20 | <10 | <10 | <20 |
| 18 Dec 1997 12:47 | <20 | **25** | <10 | **50** |
| 18 Dec 1997 12:52 | **50** | <10 | <10 | <20 |
| 18 Dec 1997 13:02 | <20 | **25** | <10 | **50** |
| 18 Dec 1997 13:26 | <20 | **25** | <10 | <20 |
| 18 Dec 1997 17:34 | **50** | <10 | <10 | <20 |
| 18 Dec 1997 17:55 | <20 | **25** | <10 | <20 |
| 22 Dec 1997 22:56 | <20 | <10 | <10 | <20 |
| 22 Dec 1997 23:40 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 00:07 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 00:47 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 01:29 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 17:31 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 17:39 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 18:01 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 18:22 | <20 | <10 | <10 | <20 |
| 23 Dec 1997 18:30 | **50** | <10 | <10 | <20 |

Numbers in bold indicate estimated values below the limit of quantification but above the limit of detection.
<20 or <10 - Below analytical limit of detection.

## 8.3 Proportional wash-off

### 8.3.1 Accumulated losses: treatment 1

| Date and time | Accumulated rainfall mm | Accumulated flow L | Accumulated loss atrazine % | Accumulated loss glyphosate % | Accumulated loss diuron % |
|---|---|---|---|---|---|
| 14 Oct 1997 16:30 | 1.2 | 10 | 0 | 0 | 0 |
| 14 Oct 1997 16:47 | 1.6 | 68 | 6 | 2 | 5 |
| 14 Oct 1997 17:25 | 2 | 154 | 19 | 9 | 16 |
| 15 Oct 1997 00:11 | 3.2 | 352 | 47 | 22 | 41 |
| 15 Oct 1997 03:27 | 4.2 | 477 | 62 | 28 | 55 |
| 15 Oct 1997 03:30 | 4.4 | 507 | 64 | 29 | 57 |
| 15 Oct 1997 03:34 | 4.6 | 533 | 66 | 30 | 59 |
| 15 Oct 1997 03:38 | 4.8 | 568 | 68 | 31 | 60 |
| 15 Oct 1997 03:42 | 5 | 599 | 69 | 31 | 61 |
| 15 Oct 1997 03:54 | 5.8 | 694 | 72 | 33 | 63 |
| 15 Oct 1997 04:24 | 6.4 | 814 | 73 | 34 | 65 |
| 15 Oct 1997 08:54 | 7.4 | 961 | 74 | 35 | 67 |
| 15 Oct 1997 09:30 | 7.6 | 1046 | 75 | 35 | 68 |
| 16 Oct 1997 10:19 | 9.6 | 1220 | 76 | 36 | 71 |
| 16 Oct 1997 10:50 | 10 | 1297 | 77 | 37 | 72 |
| 04 Nov 1997 19:07 | 13 | 1410 | 77 | 37 | 72 |
| 04 Nov 1997 20:16 | 14 | 1534 | 77 | 37 | 72 |
| 05 Nov 1997 01:50 | 15.4 | 1661 | 77 | 37 | 72 |
| 05 Nov 1997 03:28 | 16.6 | 1842 | 77 | 38 | 72 |
| 08 Nov 1997 00:16 | 18.2 | 1958 | 77 | 38 | 72 |
| 08 Nov 1997 00:42 | 19 | 2059 | 77 | 38 | 72 |
| 08 Nov 1997 01:04 | 20.2 | 2179 | 77 | 38 | 72 |
| 08 Nov 1997 01:17 | 21 | 2298 | 77 | 38 | 72 |
| 08 Nov 1997 01:54 | 22.2 | 2469 | 77 | 38 | 72 |
| 08 Nov 1997 02:18 | 22.8 | 2563 | 77 | 38 | 72 |
| 08 Nov 1997 06:50 | 24.4 | 2673 | 77 | 38 | 72 |
| 08 Nov 1997 06:52 | 24.8 | 2738 | 77 | 38 | 72 |
| 08 Nov 1997 06:54 | 25 | 2778 | 77 | 38 | 72 |
| 08 Nov 1997 06:58 | 25.4 | 2828 | 77 | 38 | 72 |

### 8.3.2 Accumulated losses: treatment 2

| Date and time | Accumulated rainfall mm | Accumulated flow L | Accumulated loss atrazine % | Accumulated loss oryzalin % | Accumulated loss oxadiazon % | Accumulated loss isoxaben % |
|---|---|---|---|---|---|---|
| 10 Dec 1997 01:07 | 2.2 | 29 | 0 | 0 | 0 | 0 |
| 10 Dec 1997 05:46 | 3.2 | 164 | 4 | 1 | 1 | 0 |
| 10 Dec 1997 06:12 | 3.6 | 239 | 7 | 1 | 1 | 0 |
| 10 Dec 1997 07:08 | 4.6 | 356 | 9 | 1 | 3 | 0 |
| 11 Dec 1997 06:05 | 6.4 | 577 | 15 | 2 | 5 | 0 |
| 11 Dec 1997 06:24 | 7 | 646 | 16 | 3 | 5 | 0 |
| 18 Dec 1997 08:56 | 11 | 703 | 19 | 3 | 5 | 0 |
| 18 Dec 1997 09:18 | 11.2 | 829 | 19 | 3 | 6 | 0 |
| 18 Dec 1997 11:54 | 12.8 | 1092 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 12:03 | 13 | 1140 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 12:34 | 13.6 | 1231 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 12:43 | 14 | 1278 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 12:47 | 14.2 | 1314 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 12:52 | 14.4 | 1352 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 13:02 | 14.8 | 1404 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 13:26 | 15.2 | 1481 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 17:34 | 16.6 | 1639 | 20 | 4 | 6 | 0 |
| 18 Dec 1997 17:55 | 17 | 1709 | 20 | 4 | 6 | 0 |
| 22 Dec 1997 22:56 | 19.2 | 1876 | 20 | 4 | 6 | 0 |
| 22 Dec 1997 23:40 | 20.2 | 1986 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 00:07 | 20.6 | 2064 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 00:47 | 21.4 | 2164 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 01:29 | 22 | 2264 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 17:31 | 23.6 | 2393 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 17:39 | 23.8 | 2440 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 18:01 | 24.4 | 2512 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 18:22 | 25 | 2581 | 20 | 4 | 6 | 0 |
| 23 Dec 1997 18:30 | 25.6 | 2632 | 20 | 4 | 6 | 0 |