Summary

Current procedures for the approval of herbicides used on land not intended to bear vegetation assumes 100% loss of herbicide from the land after 25 mm accumulated rainfall, but this assumption is not necessarily valid. The degree to which herbicides are lost from hard surfaces differs between compounds and is influenced by several factors. A previous, roadside study indicated that physico-chemical properties and the timing of rainfall following application may affect herbicide loss, but the study was not repeated (with the exception of atrazine) and did not investigate the effects of dilution in receiving water bodies.

The current study examined herbicide loss from a small urban catchment and examined herbicide concentrations in wash-off from a small, discrete sub-catchment and in the receiving water 85 m downstream from the drain outfall, after dilution had occurred. The methodology used was similar to the roadside study so the results could be compared.

The limited data suggest that herbicides of low Koc and high solubility are more susceptible to being lost following application to a hard surface (atrazine and possibly diuron). Glyphosate and atrazine were found at slightly higher concentrations in car park drainage post-15 mm of accumulated rainfall than in the roadside study. For atrazine, this was attributed to a higher percentage of the catchment being sprayed in the car park study than the roadside study, and retention within the catchment whereby atrazine was temporarily stored to be released to the aqueous phase during the next rain event. For glyphosate, the marginally elevated concentrations after 15 mm of rainfall were lower than expected given the much higher application rate. The results suggest that retention could significantly reduce glyphosate losses from hard surfaces. Comparisons for the other compounds were not possible as concentrations were all below the lowest validated level for the method of analysis. Factors encouraging herbicide retention are discussed.

The receiving ditch significantly diluted herbicides entering via the drain, but concentrations were still commonly found above 2 $\mu g L^{-1}$. It is suggested that dissipation rather than dilution alone may reduce herbicide concentrations. A peak in herbicide concentrations in the ditch was observed at the onset of heavy rainfall.

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1 INTRODUCTION

Current guidelines for determining environmental exposure to pesticides used on land not intended to bear vegetation assume that 100 % of herbicide is lost within 25 mm of rainfall. A roadside study investigating herbicide wash-off from roads (Heather *et al*., 1998) indicated that this assumption is not valid, but, that up to 80 % of an applied herbicide could be washed-off, and that the percentage wash-off differed between herbicides.

However, this initial roadside study was not replicated (with the exception of atrazine), nor did it assess herbicide concentrations in receiving ditch or stream waters where dilution and dissipation could occur. A further study was therefore undertaken to investigate the fate of herbicides applied to hard surfaces.

The aim of the follow-up study was to investigate herbicide wash-off from a small urban catchment and to quantify dilution and dissipation rates of a range of herbicides. The objectives were to:

1. Monitor herbicide concentrations in water draining from a discrete small catchment, effectively repeating the roadside study.
2. Monitor herbicide concentrations in water in a receiving ditch after dilution has occurred.
3. Quantify herbicide concentrations in a larger catchment outlet after application by contractors to give an indication of herbicide concentrations following real life applications.

The objectives effectively created two parallel studies; a ‘catchment’ study and a ‘car park’ study. The report has been divided, where appropriate, to account for both these studies.

2 SELECTION OF STUDY SITE AND TEST COMPOUNDS

A number of criteria for site selection were identified, namely that the site would:

i. be representative of a small urban catchment with a mixture of roads (asphalt and concrete kerbs), pavements (concrete slabs and/or asphalt), buildings and vegetated areas;
ii. have an outlet or outlets draining from a discrete sub-catchment with extensive hard surface cover into a receiving water course, preferably open for ease of monitoring;
iii. be sprayed by a single contractor, to enable accurate monitoring of the effects of ‘real’ spraying activities.

Permission to apply a range of pesticides from the landowners and the Environment Agency must also be granted. This was particularly important for compounds that do not have approval for use on hard surfaces (atrazine, oxadiazon, oryzalin and isoxaben) where experimental permits were required.

A site fulfilling the above criteria was identified at Cranfield University main campus in Bedfordshire (SP 940425). The catchment consisted of a mixture of buildings, hard surfaces and vegetated areas, and included a small airfield. An open ditch received water from the catchment via surface water drains, draining an area of approximately 213 ha, 27 % of which was hard surface (including roofs) and 73 % was vegetated. A car park was identified as a discrete sub-catchment draining into a single, central waste pipe discharging directly into the main drainage ditch (Car Park 1 in Figure 1). The car park consisted of an asphalt surface with concrete kerbs. The single, central drain was also constructed of concrete kerb stones. The car park perimeter and area were 149 m and 893 m^2 respectively.

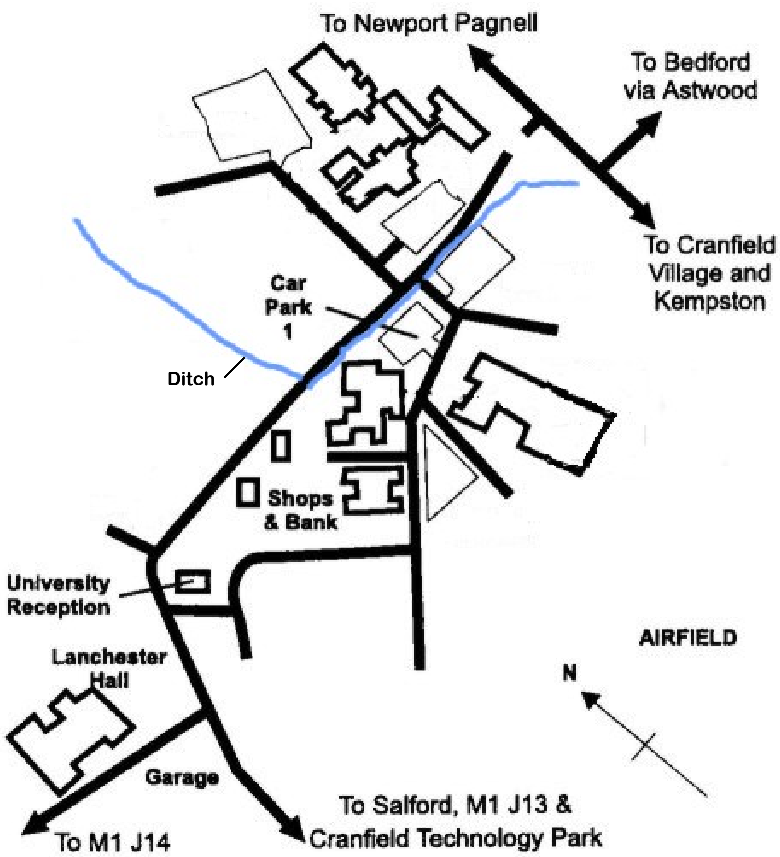

Figure 1 Position of the car park sub-catchment within Cranfield University campus

The behaviour of a number of compounds was investigated in the study (glyphosate, atrazine, diuron, oxadiazon, oryzalin and isoxaben). These provided a broad range of physico-chemical properties and were the same compounds as those used in the earlier roadside study, thus enabling comparison with its results.

3 CATCHMENT STUDY

The objective of the catchment study was to observe normal practices and to quantify herbicide concentrations in a catchment outlet, after application by contractors, to give an indication of herbicide concentrations following real life applications. This was achieved by interviewing the contractors and observing application practices, and subsequent monitoring of the drainage ditch (Figure 1) for the catchment.

3.1 Herbicide application

The contractors applied herbicide to the whole catchment (excluding the car park) on 17th April 1999. The compound used was MSS Diuron 50FL. This was poured into a graduated beaker before being transferred to a 15L knapsack and water added. Filling was confined to a single place within the work shed. A total of 6 knapsacks were used to spray the Cranfield campus. The area sprayed was to be calculated retrospectively in collaboration with the contractors.

The spray in April was one of 2 or 3 planned for the year (depending on the success of each spray).

3.2 Sampling methodology

Infrastructure plans were used to identify surface sewer inputs to the ditch from Cranfield campus. A suitable section of the ditch, approximately 5 m downstream from the last sewer outfall (SP 942431), was instrumented to monitor water dynamics in the ditch. Existing records of flow estimates for the drainage ditch indicated that any construction, such as a weir, would have to be a substantial size, and that this could cause water to back up to unacceptable levels upstream. A Starflow, consisting of a pressure transducer, doppler and internal logger, was therefore used to measure flow in the drainage ditch. This was set to record discharge every 10 minutes. An Epic automatic water sampler was used to collect ditch water samples. A tipping bucket raingauge was sited in an open field 5 m from the ditch and connected to the data logger. The data logger was configured to trigger the water sampler to collect samples at the onset of rainfall, every millimetre of rainfall for the first 10 mm of rain, and then every 2 mm of rainfall until 25 mm of rain had fallen. A sample would also be taken 30 minutes after the first trigger, if a millimetre of rain had not fallen.

It was intended that the sampling equipment be tested prior to the contractors spraying. However, whilst the equipment was being installed only one day's notice was given of a change in spray schedule, prohibiting the testing of the equipment.

3.3 Amendment to the sampling site

Unforeseen construction work, affecting the flow of the drainage ditch, commenced within the Cranfield campus during the study period. This occurred after the contractors had sprayed the catchment, and, because the catchment would not be sprayed again within the timescale of the study, the catchment study was terminated.

3.4 Results

Observation of the contractors during herbicide application indicated that there were slight differences in practices between the two workers with one spot spraying more than the other. In general, areas were band sprayed only where required, with spot spraying acknowledged as being more economical.

No results are available for herbicide concentrations following a real spray event due to an initial malfunction of the water sampler and subsequent disturbance of the original sampling point (sections 3.2 & 3.3).

The results and discussion contained within this report therefore relate to the car park study alone.

4 CAR PARK STUDY

4.1 Application of test compounds

The six test herbicides were applied to the car park by SSLRC staff using a 'Vermorel 2000 HP' 20 l knapsack sprayer, fitted with a 02E80 nozzle. The required amount of each herbicide and water was measured out the day prior to application. On the day of application, after pouring herbicide solution into the knapsack, the vessel containing the concentrate was repeatedly rinsed with water assigned for dilution, and poured into the knapsack. The knapsack was shaken before spraying commenced. Each herbicide was prepared and applied individually.

The kerb edge of the car park (149 m) was sprayed in a continuous swath, approximately 27.5 cm wide, as were both edges of the central drain (21.3 m in length). The land sprayed consisted of asphalt and concrete kerb. The central drain was made from two kerb stones flush with the asphalt surface with a 0.1 m gap between them enabling water to drain through. Consequently, the area sprayed around the central drain also consisted of concrete and asphalt. The car park was not swept prior to herbicide application and organic debris was visibly present within the area sprayed. One gully was present in the edge of the car park. Care was taken to ensure that only the edges of the iron grille, and not the grille itself were sprayed. Two parked cars prevented application on a small section of kerb (circa 4m). The total area sprayed was approximately 53 m^2.

The quantities applied of each herbicide were as directed on the product label. Any small quantities of herbicide left in the knapsack were sprayed into a marked, weighed bottle. On returning to the laboratory, the bottles were re-weighed to determine the remaining amount of herbicide solution, enabling the actual amount of herbicide applied to be quantified (Table 1).

	Glyphosate	Diuron	Oxadiazon/ Glyphosate	Atrazine	Oryzalin	Isoxaben
Application rate (Lha^{-1})	5	5.4	15	6	3.6	0.6
A.S. (gL^{-1})	360	500	300/108	500	480	125
Active applied (g) Spray 1	18.20*	12.43	22.40	16.26	9.22	0.40
Active applied (g) Spray 2	19.06*	16.05	25.31	16.09	9.65	0.41

* This is a total concentration and accounts for glyphosate present with oxadiazon.

Table 1 Summary of herbicide application rates and quantities actually applied

Both the knapsack and the spray line were rinsed thoroughly with water between applications, and the rinsings were disposed of elsewhere.

The car park was sprayed on two occasions – 27 May 1999 and 9 June 1999 – with approximately 60 mm rainfall between application dates.

4.2 Sampling methodology

4.2.1 Car Park Outlet

A small, 90° weir box, with pressure transducer, was used to monitor flow from the car park drain. The weir box was calibrated in the laboratory to produce a transducer reading:discharge rating curve (r^2 = 99.7 %). Gauze was placed over the drain outfall and in front of the weir plate to prevent sediment accumulating in the weir box and to prevent erosion of the plate. However, after the first major rain event, sufficient fine sediment had built up to affect the calibration curve. Discharge was subsequently calculated using knowledge of the time taken for each 0.2 mm of rain to fall, and the catchment area. It was assumed that only 95 % of rain would appear as runoff; This assumption is the same as was used in the roadside study.

Water was collected for analysis after flowing over the weir by an Epic automatic water sampler. A data logger was configured to trigger the water sampler to collect samples at the onset of rainfall, every millimetre of rainfall for the first 10 mm of rain, and then every 2 mm of rainfall, until 25 mm of rain had fallen. A sample would also be taken 30 minutes after the first trigger, if a millimetre of rain had not fallen.

Rainfall was monitored using a tipping bucket rain gauge (linked to the data logger) sited on the edge of the car park and air temperature was recorded at Silsoe College, approximately 13 miles away.

4.2.2 Drainage Ditch

The car park outlet drained directly into the drainage ditch (Figure 1). A monitoring point was established 85 m downstream from the car park outfall. This distance is comparable to the standard stream length of 100 m used in the First Tier Surface Water Exposure, thus the results could be used for validation purposes.

An Epic automatic water sampler was used for the collection of water samplers. This was triggered by the same logger, and in the same manner as for the car park outlet (section 4.2.1). A Starflow (section 3.2) was used to calculate discharge.

Samples were removed from the collection vessels as soon as practical after a rain event (usually the following day). Samples were decanted into vessels appropriate to the herbicide of interest, namely; glass – atrazine, diuron and oxadiazon; amber glass – isoxaben and oryzalin; HDPE – glyphosate, and either stored frozen (glyphosate) or refrigerated (atrazine, diuron, oxadiazon, oryzalin and isoxaben), before being dispatched to the relevant company for analysis.

Control grab water samples were taken prior to herbicide application on 26th May 1999 and 8th June 1999. These samples were decanted and stored in the same manner as those collected by the automatic water samplers.

4.3 Analysis

The herbicides were analysed by several companies using different methods, developed and documented by the individual company laboratories. The levels of detection and validation differed between herbicides, and are tabulated below. The lowest validated level (LVL) was 5 times the limit of detection.

	Analytical Company	Detection limit (μgL^{-1})	Lowest Validated Level (μgL^{-1})
Atrazine	Aventis	10	50
Diuron	Aventis	10	50
Oxadiazon	Aventis	20	100
Glyphosate	Huntingdon Life Sciences	0.01	0.05
Isoxaben	Dow AgroSciences	2	10
Oryzalin	Dow AgroSciences	2	10

Table 2 Lower validation and detection limits of compounds analysed

In Section 3 and 4, reference is made to concentrations reported below the level of validation but above the limit of detection. Emphasis should be placed on the order of magnitude, rather than the exact value where these figures are reported, because the values are estimates (as determined by the analytical companies) and could not be validated.

5 RESULTS

Despite frequently testing the equipment in the field, there were several occasions when the automatic water sampler did not function, including the first rain event after the contractors had sprayed the catchment.

In order to maximise the information from the study, selected samples were targeted for analysis. Samples were selected to provide limited data for comparison of car park wash-off results with those from the roadside study. Data enabling quantification of dilution for the catchment was very limited.

5.1 Rainfall and Air Temperature

Within a week of herbicide application to the car park, 59 mm of rain had fallen and this was confined primarily to two days (13 mm on 30 May and 45 mm on 2 June). The rain events were typical summer storms. Throughout the rest of June, rain events were minor both in magnitude and frequency (Figure 2).

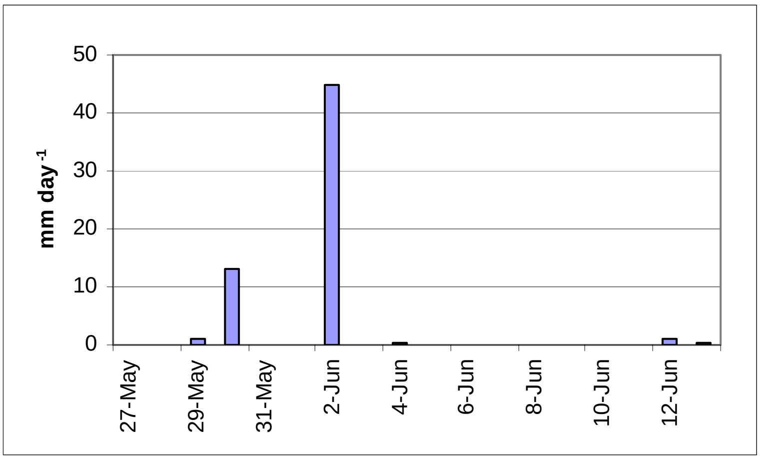

Figure 2 Daily rainfall at Cranfield University during the study period

Air temperature averaged 14 °C throughout the study period and fluctuated diurnally. Maximum temperatures were higher at the end of May than the beginning of June, but average temperatures for both months were very similar (Figure 3).

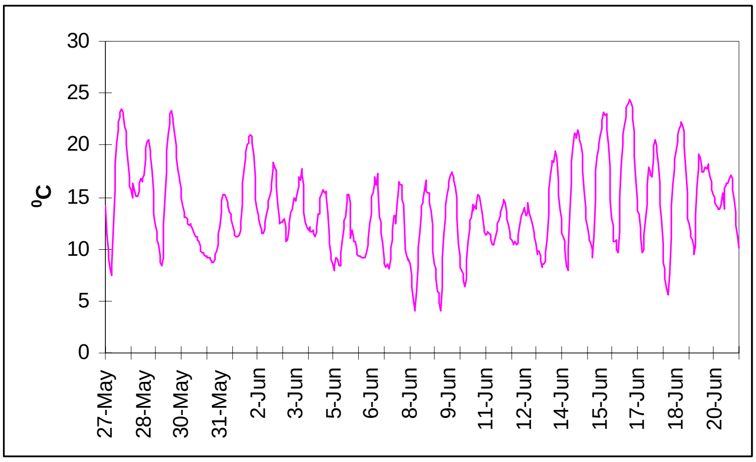

Figure 3 Hourly air temperature at Silsoe during the study period

5.2 Discharge in the drain and ditch

Discharge in the drain and ditch is illustrated in Figure 4 -Figure 7. Maximum discharge from the ditch during the first rain event was close to 9 ls^{-1} (Figure 4), less than half of the maximum discharge during the second rain event (21 ls^{-1}, Figure 5). In comparison, the rain event of 12 June 1999 was minor with discharge remaining below 1 ls^{-1} (Figure 6). This pattern reflects the total rain in each event (section 5.1).

The ditch rapidly responded to rainfall (Figure 7) with maximum discharge during the storm of 2 June 1999 in the order of 1200 ls^{-1}. (The Starflow aborted recording discharge between 30 May and 2 June, hence the apparent lack of discharge in the ditch in response to rainfall).

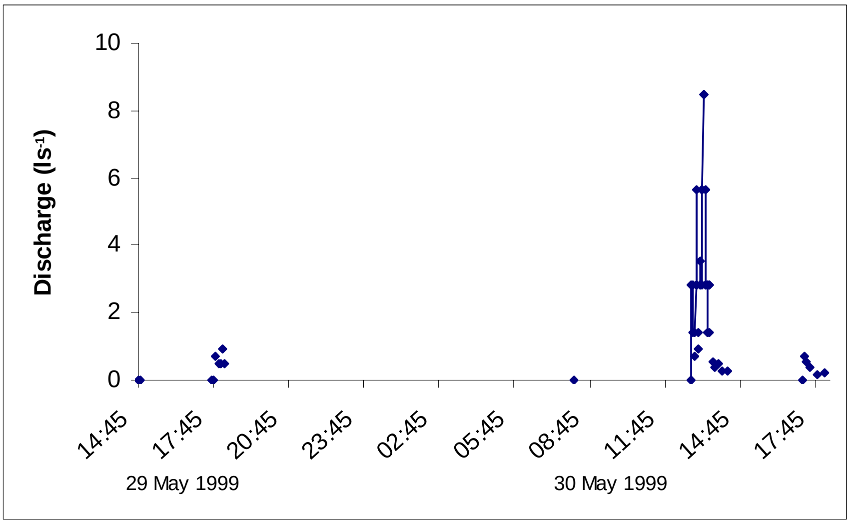

Figure 4 Discharge from the car park drain, 29 & 30 May 1999

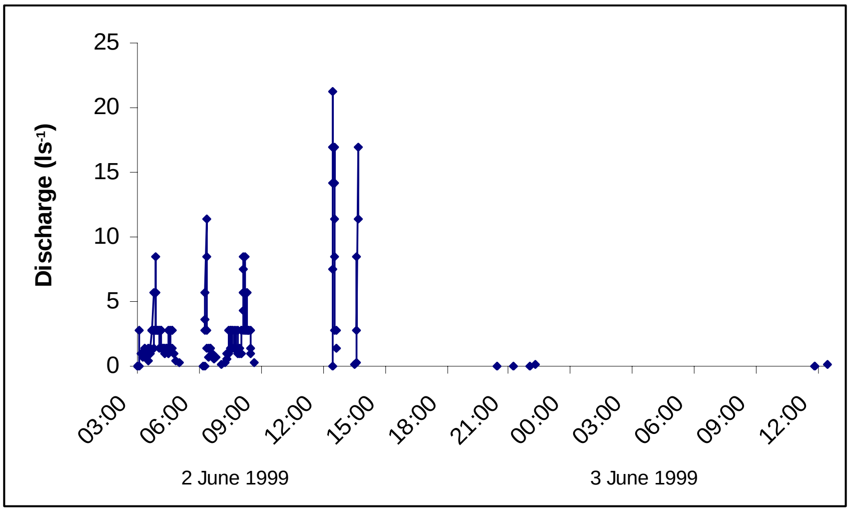

Figure 5 Discharge from the car park drain, 2 & 3 June 1999

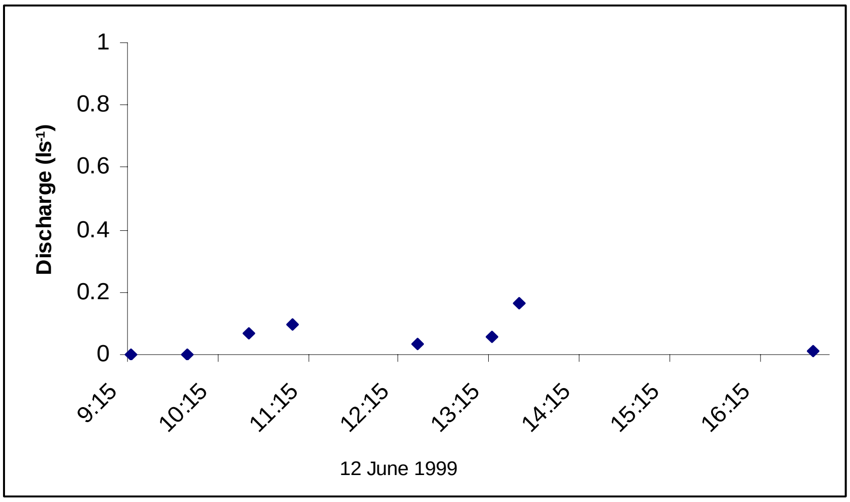

Figure 6 Discharge from the car park drain, 12 June 1999

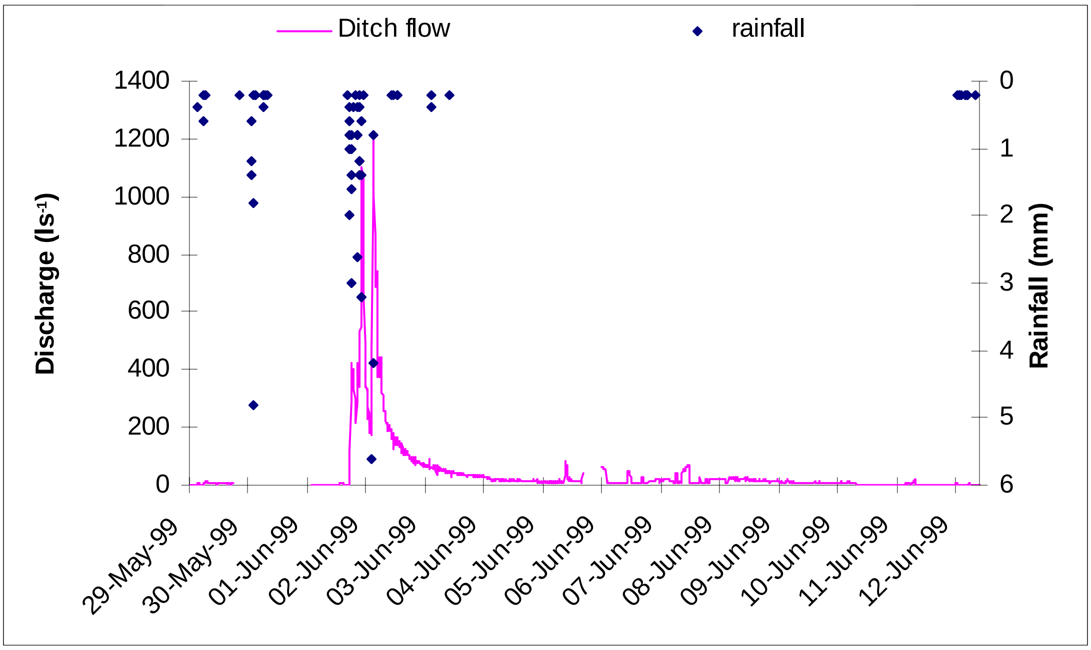

Figure 7 Discharge in the ditch in response to rainfall

5.3 Herbicide Concentrations

The car park was sprayed twice in an attempt to obtain more data to achieve the aims of the study. Control samples taken before the second spray contained atrazine and diuron at mean concentrations of 69 μgL^{-1} and 26.5 μgL^{-1} respectively. Oryzalin was also detected. The mean oryzalin concentration was calculated from given values as 2.5 μgL^{-1}, however, as the values given were below the LVL, this figure must be treated with caution. Isoxaben was not detected above 2 μgL^{-1}.

Details of herbicide concentrations for all samples analysed are given in Appendix 1.

5.3.1 Car Park Outlet

No wash-off data are available during the first 15 mm of rainfall due to equipment failure. However, between 15 and 20 mm, and after 59 mm of accumulated rainfall some data provide useful information.

A comparison is made below of herbicide concentrations after 15 mm of rainfall in the current and the roadside study (Figure 8 to Figure 13(note the difference in scales) and Table 1).

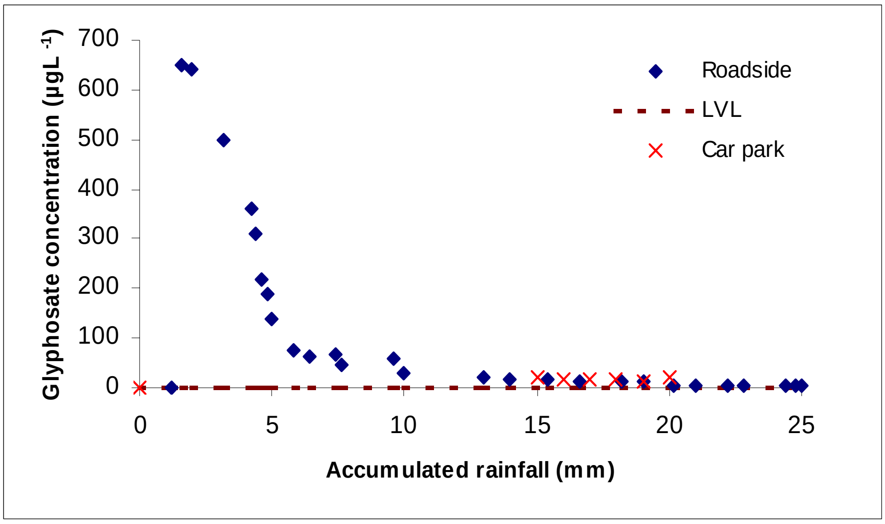

Figure 8 Glyphosate concentrations in wash-off from the car park and the roadside studies.

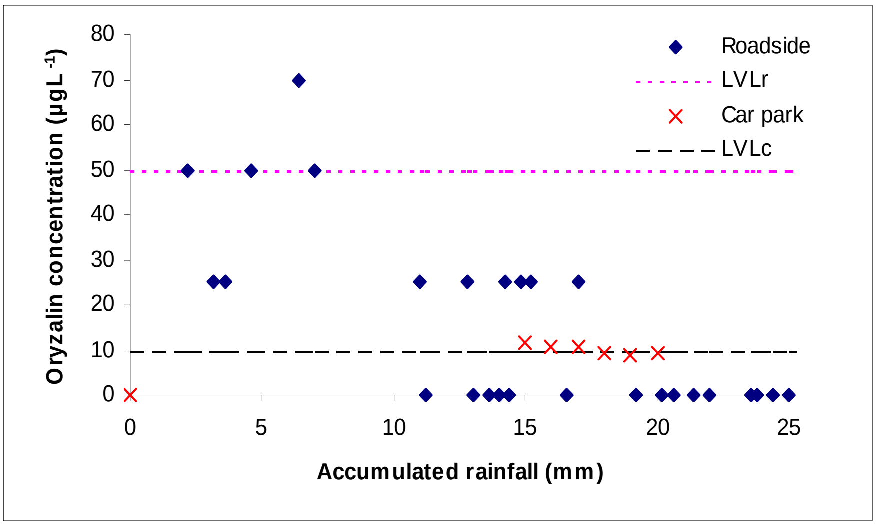

Figure 9 Oryzalin concentrations in wash-off from the car park and the roadside; LVLr = roadside study LVL, LVLc = car park study LVL studies

Note: Oryzalin concentrations of '25 μgL^{-1}' from the roadside study were in reality half the LVL (50 μgL^{-1}) thus these points could lie anywhere between 10 – 50 μgL^{-1} and therefore could be below, or more similar to concentrations found in the car park drainage water.

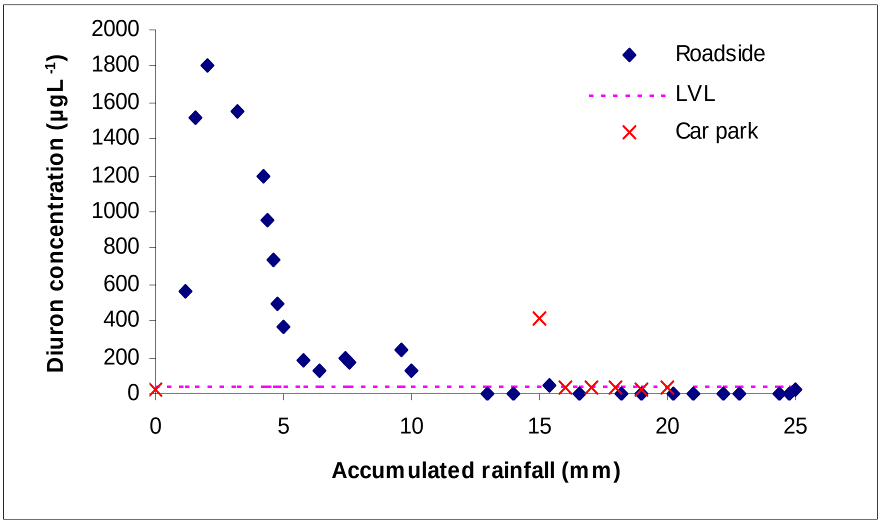

Figure 10 Diuron concentrations in wash-off from the car park and the roadside studies

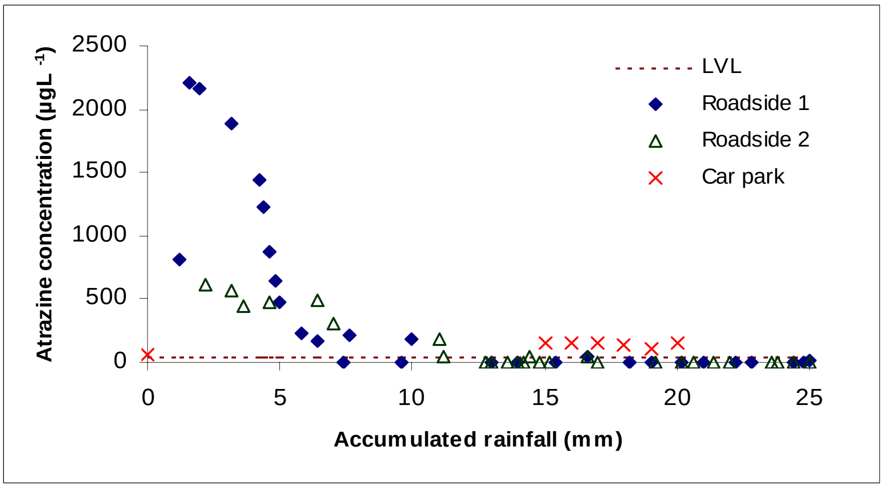

Figure 11 Atrazine concentrations in wash-off from the car park and the roadside studies

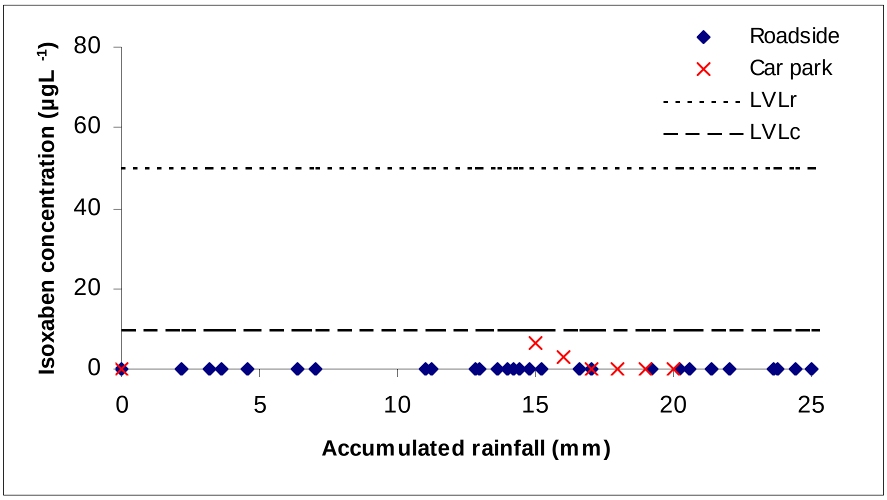

Figure 12 Isoxaben concentrations in wash-off from the car park and the roadside; LVLr = roadside study LVL, LVLc = car park study LVL studies

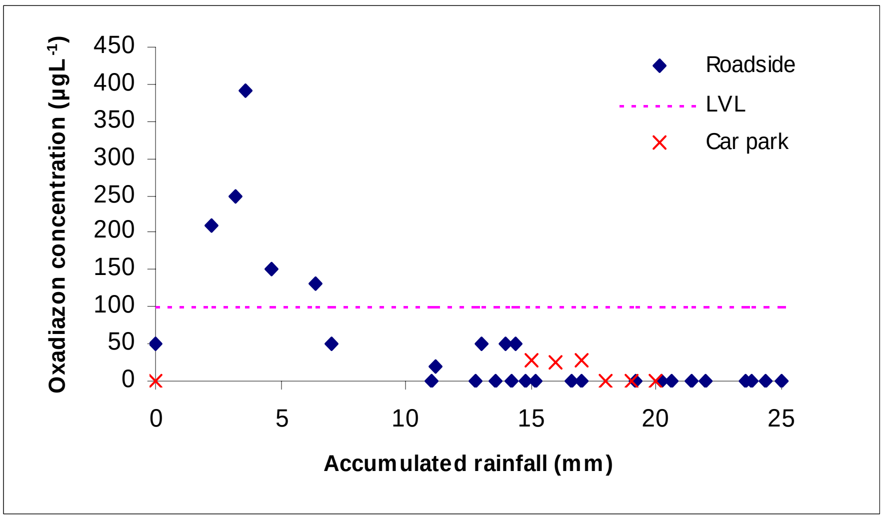

Figure 13 Oxadiazon concentrations in wash-off from the car park and the roadside studies

Glyphosate concentrations in car park wash-off between 15 and 20 mm of accumulated rainfall remained similar and were marginally higher, but of the same order of magnitude, as found in the roadside study (Figure 8). Mean glyphosate concentrations between 15 mm and 20 mm accumulated rainfall being 11.4 and 16.7 μgL^{-1} for the roadside and car park study respectively.

A similar pattern was observed for atrazine, although exact comparisons with the roadside study are more difficult because of values below the LVL. Between 15 and 20 mm of rainfall, atrazine concentrations in washoff from the car park remained between 110 and 160 μgL^{-1}, whereas equivalent values for the roadside study were less than 50 μgL^{-1} (Figure 11).

In contrast to glyphosate and atrazine, all the other compounds applied appear to show a general decrease in runoff concentrations between 15mm and 20mm of rainfall (Figures 9,10,12 & 13), although it is not possible to quantify this accurately as most measured concentrations were either below the LVL or below the limit of detection. Because of this, and because, for some compounds the roadside study had a higher LVL (and hence higher limit of detection) than the car park study, quantifiable comparisons of the two are not possible. Table 3 shows the comparison of measured herbicide concentrations between 15 and 20 mm accumulated rainfall for both the car park and the roadside studies.

It was not possible to determine percentage loss of active substances due to missing data.

	Max concentration (μgL^{-1}) between 15 and 20 mm accumulated rainfall		Mean concentration (μgL^{-1}) between 15 and 20 mm accumulated rainfall	
	Car park	Roadside	Car park	Roadside
Glyphosate	19.3	16	16.7	11.4
Oryzalin	10	<50	10	< 50
Diuron	410	<100	97 (35)*	<100
Atrazine	160	<100	148	<100
Isoxaben	<10	<10	<10	<10
Oxadiazon	27	<60+	18.2#	<20

*The mean diuron concentration excluding the peak concentration of 410 μgL^{-1} is given in parentheses. In the roadside study, there was no obvious peak as in the current study. + A ‘mean’ of <100 and <20 contained in samples taken at 14.8 and 15.2 mm of accumulated rainfall respectively. # This includes 3 samples containing concentrations <20 μgL^{-1} which have been assigned concentrations of 10 μgL^{-1} for the purposes of the calculation.

Table 3 A comparison of herbicide concentrations between the roadside and the car park study for 15 to 20 mm accumulated rainfall

5.3.2 Drainage Ditch

In the receiving ditch, with the exception of glyphosate, herbicide concentrations remained below their lower validation limit, thus a dissipation factor could not be determined. Oryzalin, atrazine and glyphosate were present at concentrations above the detection limit, and estimates of herbicide concentrations were given where these were below the LVL, thus some inferences could be made as to the fate and behaviour of these herbicides, but with varying degrees of confidence. Isoxaben, oxadiazon and diuron all remained below the limit of detection in the drainage ditch for the duration of the study, as discussed below.

From the limited data available for herbicide concentrations in the ditch, it appears that herbicide concentrations increase at the onset of heavy rainfall (Figure 14).

There is a very short lag time between the apparent maximum atrazine concentration in the ditch and the onset of heavy rainfall. Within 23 minutes 3.2 mm of rain fell (accumulated rainfall = 5.2 mm), after which atrazine concentrations in the ditch peaked. Following a further, 5 mm of rain in 12 minutes (accumulated rainfall = 10.6 mm), oryzalin and glyphosate concentrations also peaked. Diuron, oxadiazon and isoxaben concentrations in the ditch were all below the limit of detection. However, it should be noted that these limits were 10, 20 and 2 μgL^{-1} respectively. Oryzalin and glyphosate concentrations actually measured in the ditch were all below the equivalent concentration of the limit of detection for diuron and oxadiazon.

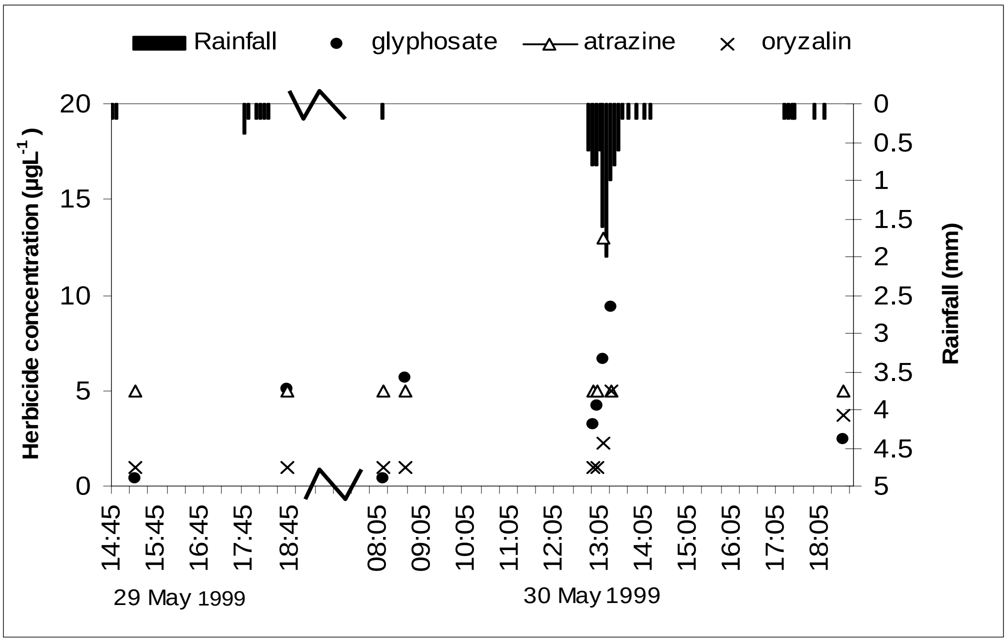

Figure 14 Herbicide concentrations in ditch water during the first rain event following application. (Where atrazine and oryzalin concentrations were below the limits of detection; 10 and 2 μgL^{-1} respectively, concentrations are plotted at 5 and 1 μgL^{-1} respectively).

6 DISCUSSION

6.1 Wash-off from the car park

6.1.1 Comparison with the roadside study

A comparison of the results from the current study and those of the roadside study indicate that the order of magnitude of herbicide losses was generally similar in both studies. As described in section 3.4.1, quantitative comparisons are only possible for glyphosate and atrazine and for both these compounds, the results suggest that concentrations between 15 and 20 mm of accumulated rainfall are larger in the current study than in the roadside study. It is possible that this is also the case for diuron, but the data for the car park study is very heavily influenced by a single analysed sample value of 410 μgL^{-1} which gives a washoff pattern in contrast to the data for all the other compounds. For oryzalin, isoxaben and oxadiazon, no quantitative comparisons are possible because of the relatively large levels of analytical validation and detection in one or both studies.

The slightly higher concentrations observed after 15 mm of rainfall in the current study may have a number of possible explanations. Firstly, in the roadside study, Zapper and Roundup were applied on different spray dates, unlike in the car park study. Consequently, the application rate of glyphosate for the car park study was almost double that for the roadside study (3430 and 1800 g ha^{-1} respectively). This may explain the slightly larger measured glyphosate concentrations after 15 mm of rainfall from the car park drain although, given that the application rate was almost double, it would be expected that the glyphosate concentrations would be much larger than those actually measured.

Secondly, although the application rate was the same between studies for all other compounds, a higher percentage of the total catchment area was sprayed in the current study, compared to the roadside study (5.9 % and 4.3 %, respectively (Table 4)). If it is assumed that washoff patterns in the current study are the same as in the roadside study, then it would be expected that herbicide concentrations after 15 mm of rainfall would be 1.37 times (the ratio of the percentages of the catchment sprayed) greater in the car park drainage. However, atrazine concentrations in car park drainage are a *minimum* of 1.49 times greater than in roadside drainage after 15 mm of rainfall.

	Car park	Roadside
Catchment area (m^2)	893	112
Area Sprayed (m^2)	53	4.8
Percent area sprayed %	5.9	4.3

Table 4 A comparison of the areas sprayed in the car park and roadside studies

This higher loss of atrazine than ‘expected’ after 15 mm of rainfall in the car park study may be due to a combination of factors. Firstly, rain falling between 15 and 20 mm of accumulated runoff in the car park study was at an equivalent intensity of 7.5 mmh^{-1}. This compares to the roadside study where the maximum intensities were less than 3 mmh^{-1} after 15 mm of accumulated rainfall.

The second explanation for greater concentrations of atrazine measured in the car park drain after 15 mm of rainfall is the possibility that more herbicide was retained within the car park (with a corresponding decrease in loss) between 0 and 15 mm of accumulated rainfall, than in the roadside study. Any retained herbicide would then potentially be available for washoff at the onset of further rain.

(Both these processes could also contribute to glyphosate dynamics, although glyphosate concentrations post-15 mm of rainfall were lower than ‘expected’).

The reason for this apparent greater retention of atrazine (and possibly other compounds) within the car park study may relate to differences in the size and shape of the two catchments (see Table 4 and Figure 1). For a significant proportion of those compounds applied to the car park, the distance between the herbicide source and the drain outfall was considerably longer than in the roadside catchment. The maximum distance between herbicide source and the drain outfall was approximately 43 m in the car park study and 15 m in the roadside study. It is possible that this results in longer ‘travel times’ to the car park drain, requiring significantly greater amounts of accumulated rainfall before the compounds are washed out of the catchment.

An additional factor that may contribute to the apparently greater retention of herbicides in the car park study, is sorption to hard surfaces and organic / dust particles within the catchment. The roadside was swept before herbicide application whereas in the car park, this was not the case and a build up of particulate matter (e.g. soil, vegetation and dead leaves and other organic material) was noted around its edges. More adsorption sites may therefore have been available in the catchment study than the roadside study. For strongly sorbed compounds such as glyphosate and oxadiazon, this may result in permanent retention within the catchment, or loss only via particulate wash-off. Such a mechanism may explain the smaller than expected concentrations of glyphosate measured in run-off from the 15 to 20 mm of accumulated rainfall in the car park sub-catchment.

In contrast, for weakly sorbed compounds such as atrazine and diuron, sorption on particulate material during aqueous transport in runoff from initial rainfall events could result in ‘temporary storage’ within the catchment. Later rainfall events would result in ‘fresh’ surface water flowing over the particulate material, resulting in desorption of some previously sorbed compound and further aqueous losses. By this mechanism, catchments with significant amounts of particulate material would appear to ‘retain’ weakly sorbed compounds for longer periods than would relatively ‘clean’ catchments.

The above discussions are based on the assumption that herbicide behaviour was similar during 0 and 15 mm of accumulated rainfall between the roadside and current study. Natural variations between sites and the opposing seasons in which the studies were conducted (late autumn and early summer respectively) may also influence the results. Confidence in the interpretation of the results is therefore limited.

6.1.2 Comparison with herbicide properties

Mean herbicide concentrations between 15 and 20 mm of rainfall were compared to Koc, solubility and application rate using multiple regression to determine whether or not any relationships existed. (Oxadiazon and isoxaben were ‘not detected’ for some sampling events after 15 mm of rainfall and, in the analysis below, values for half the detection limit were used, i.e. values of 10 and 1 μgL^{-1} respectively). It is emphasised that the data set used to establish relationships consisted of only 5 points, was thus very limited and the results are not conclusive, but may be indicative of possible patterns in the data. A single extreme value could greatly influence the outcome of a regression, and it is to this end that glyphosate was excluded from the data set due to its extreme values for solubility and Koc.

These limited data suggest that, for the 5 compounds analysed, solubility was the most significant factor determining mean concentrations in runoff from the car park between 15 and 20 mm of accumulated rainfall ($r^2 = 86.8$, $p < 0.05$).

6.2 Herbicides in the receiving ditch

Herbicide concentrations observed in the ditch differed temporally between herbicides. For example, after 14.2 mm accumulated rainfall (following the short, intense rain event (section 5.3.2)), glyphosate and oryzalin concentrations in the ditch were 2.4 and 3.7 μgL^{-1} respectively. However, after 58 mm of rain had fallen, glyphosate concentrations had decreased to 0.1 μgL^{-1}, whereas oryzalin concentrations were 2.5 μgL^{-1}. These results suggest that glyphosate is either degraded or readily removed from solution, probably because of its high Koc, which is of more relevance in the ditch containing sediment and organic matter than on the hard surface.

In relation to the other applied herbicides, the concentrations of oryzalin and glyphosate in the ditch were all below those equivalent to the limit of detection for atrazine, diuron and oxadiazon, which could have been present at higher concentrations than oryzalin and glyphosate. Likewise, isoxaben may or may not have been present at higher concentrations than glyphosate after 58 mm of rainfall.

The limited data suggest that dilution and/or dissipation in the receiving ditch is significant and reduces direct runoff concentrations by at least 7 times. For example, atrazine concentrations decrease from 77 μgL^{-1} in drainage from the car park to < 10 μgL^{-1} at the ditch monitoring point (see appendix). No further inferences regarding dilution and dissipation can be made from the data available.

7 CONCLUSIONS

- In relation to environmental quality standards, atrazine and diuron were found at relatively high concentrations (> 100 and 20 µgL^{-1} respectively) in car park wash-off after 15 mm of accumulated rainfall. This compares with the roadside study where greater amounts of atrazine and diuron were lost relative to glyphosate, oxadiazon, oryzalin and isoxaben.

- Concentrations of glyphosate in drain flow after 15 mm of rainfall were similar in both the car park and the roadside study, despite the difference in total herbicide applied. Retention by organic/particulate matter or the hard surface itself may be important to glyphosate loss from hard surfaces.

- Atrazine concentrations in drain flow were greater in the car park study than the roadside study after 15 mm of rainfall. This was attributed to a higher percentage of the catchment being sprayed in the car park study, and possible longer travel times, hence greater temporary retention in the car park catchment, rendering more available for loss after 15 mm of rainfall.

- Limited statistical analysis suggests that solubility may be an important factor in controlling the loss of herbicides from hard surfaces.

- Herbicide concentrations in runoff from the car park appear to be significantly diluted during transport in the receiving ditch water, but during a rain event, atrazine, oryzalin and glyphosate concentrations peaked to 5 µgL^{-1} or more. Isoxaben concentrations remained below 2 µgL^{-1} and diuron and oxadiazon below 20 µgL^{-1}.

- After 58 mm of accumulated rainfall, glyphosate concentrations were 0.1 µgL^{-1}, whereas oryzalin concentrations remained elevated (2.5 µgL^{-1}). Atrazine, diuron and oxadiazon may have been present at higher concentrations than those measured for oryzalin and glyphosate, but this could not be confirmed or refuted because of their relatively high limits of detection. Isoxaben concentrations were equal to or below 2 µgL^{-1}, but could not be further quantified.

8 RECOMMENDATIONS

The results of the catchment study show that, despite more herbicide per unit area being applied, herbicide concentrations in drain water were similar in both the roadside and car park study. Two herbicides, characterised by relatively high solubilities and low K_{oc}s (atrazine and diuron), were found at marginally higher concentrations.

The processes of herbicide retention and/or degradation need examining before a full understanding of wash-off from hard surfaces can be achieved. This includes investigation of:

- herbicide partitioning to, and release from, hard surface materials.

- herbicide partitioning to, and release from, sediment material associated with hard surfaces

- the effect of temperature on degradation of retained herbicides.

- the effect of adjuvants on herbicide wash-off.

Due to inter- and intra-site variations (the latter largely climatic), more confidence in results could be obtained if a study was conducted where more than one site was monitored over several seasons. This would allow for natural spatial and temporal variations that occur in field-scale studies and could confirm, or otherwise, the hypotheses presented in this report.

In relation to dilution of wash-off by receiving water, the kinetics of herbicide sorption to sediment should be investigated, together with the ecotoxicological effects of intermittent and short-lived peaks in herbicide concentration.

9 REFERENCE

Heather A.I.J., Shepherd, A.J. and Hollis, J.M. (1998). Losses of Six Herbicides from a Kerb-and-Gully Pot Road Drain. Soil Survey & Land Research Centre Report.

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11 APPENDIX – MEASURED CONCENTRATIONS OF HERBICIDE

		Herbicide Concentration (µgL^{-1})						
		Accum rainfall	Atrazine	Diuron	Oxadiazon	Oryzalin	Isoxaben	Glyphosate
CP1	29/05/99 15:17	0	61	*19*	< 20	< 2	< 2	0.2
CP2	02/06/99 03:14	15	160	410	*27*	11.7	*6.6*	19.3
CP3	02/06/99 03:32	16	160	*40*	*25*	10.5	*3.1*	16.4
CP4	02/06/99 03:42	17	160	*37*	*27*	10.6	< 2	16.6
CP5	02/06/99 03:46	18	140	*32*	< 20	*9.3*	< 2	15.1
CP6	02/06/99 03:51	19	110	*27*	< 20	*9*	< 2	14.2
CP7	02/06/99 03:54	20	160	*38*	< 20	*9.4*	< 2	18.9
CP10	control		74	*27*	< 20	*5*	< 2	5.8
CP11	control		64	*26*	< 20	*5*	< 2	4.1
CP14	12/06/99 09:46	59.2	70	*23*	*25*	< 2	< 2	
CP15	12/06/99 10:24	59.4	58	*18*	*26*	< 2	< 2	3.3
CP16	12/06/99 11:34	59.8	75	*23*	*28*	< 2	< 2	3.4
CP17	12/06/99 12:28	60	77	*24*	*29*	< 2	< 2	
CP18	12/06/99 12:57	60.2	74	*24*	*30*	< 2	< 2	
DS1	29/05/99 15:17	0	< 10	< 10	< 20	< 2	< 2	0.4
DS3	29/05/99 18:41	2	< 10	< 10	< 20	< 2	< 2	5.1
DS2	30/05/99 08:09	2.2	< 10	< 10	< 20	< 2	< 2	0.4
DS4	30/05/99 08:38	2.8	< 10	< 10	< 20	< 2	< 2	5.7
DS5	30/05/99 12:53	3	< 10	< 10	< 20	< 2	< 2	3.2
DS6	30/05/99 13:01	4	< 10	< 10	< 20	< 2	< 2	4.2
DS7	30/05/99 13:09	5	*13*	< 10	< 20	*2.2*	< 2	6.6
DS8	30/05/99 13:21	10	< 10	< 10	< 20	*5*	< 2	9.4
DS9	30/05/99 18:35	14.2	< 10	< 10	< 20	*3.7*	< 2	2.4
DS14	control		< 10	< 10	< 20	*2.4*	< 2	0.1
DS15	control		< 10	< 10	< 20	*2.6*	< 2	0.1
DS16	12/06/99 11:34	59.8	< 10	< 10	< 20	*3.8*	< 2	
DS17	12/06/99 12:28	60	< 10	< 10	< 20	*3.7*	< 2	0.2
DS18	12/06/99 12:57	60.2	< 10	< 10	< 20	< 2	< 2	0.5
DS19	12/06/99 14:04	60.4	< 10	< 10	< 20	*2.2*	< 2	1
DS20	12/06/99 17:19	60.8	< 10	< 10	< 20	*2.6*	< 2	0.1

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