

## Summary

Six herbicides (atrazine, diuron, oxadiazon, glyphosate, oryzalin, isoxaben), selected to represent a range of physico-chemical properties and application rates, were applied separately, via a knapsack sprayer to a former railway test track at Hilton. All rail tracks at the site had been removed and only the ballast for a single track was still in place. Sampling of drainage waters from the formation was carried out from three trenches dug through the ballast into the underlying 'soil' formation at the side of the single-track bed. These trenches were labelled 'upper', 'middle' and 'lower' according to their location on the gradient and water that collected in them was 'grab' sampled using HDPE bottles. Water samples from the trenches were collected on 11 occasions between 4 and 81 days after herbicide application, normally in response to specific rainfall events. In addition, samples from the 'soil' formation beneath the railway ballast adjacent to the 'middle' and 'lower' surface water trenches were taken for analysis 33 days after application and from the 'soil' formation adjacent to the 'upper' trench 83 days after application. There was a significant rainfall event on the second day after application and subsequent rainfall was unusually large for the time of year. 25 days after application, 81.8 mm of rain had fallen on the site whilst by the end of the study, 83 days after application a total of 153mm of rain had fallen.

Apparent positive but unquantifiable detections of glyphosate, oxadiazon, isoxaben and oryzalin in control waters sampled from a small, specially dug hole the day before herbicides were applied made interpretation of the analytical data difficult. This was compounded by the relatively high analytical validation levels for all compounds except glyphosate. Nevertheless, unequivocal quantifiable concentrations of atrazine, diuron and glyphosate were found in almost all of the water samples taken. Maximum detected concentrations ranged from 1097  $\mu\text{g l}^{-1}$  for atrazine to 12.4  $\mu\text{g l}^{-1}$  for glyphosate and, for all three sampling trenches, always occurred in the second sample, taken 6 days after application. These peaks appear to be the result of rainfall events occurring 2 to 3 days earlier and are not present in drainage water samples taken in response to those events. There thus appears to be a significant 'time lag' between rainfall events and herbicide movement to surface waters in response to those events. Subsequent sampling showed other smaller concentration peaks on some occasions in most drainage ditches, but the pattern was not consistent for all compounds.

Accurate calculation of accumulated % losses from the railway study is not possible because drainage flows were not measured. However an approximate calculation was made based on a set of assumptions for drainage fluxes through the ditches. These crude estimates give accumulated percentage losses of 12.3 % for atrazine, 1.3% for diuron and 0.1% for glyphosate. However, on the last sampling occasion, 81 days after application, when only the upper trench was sampled, glyphosate was detected at a concentration of 0.8  $\mu\text{g L}^{-1}$ , atrazine was detected at the lower validation concentration of 10  $\mu\text{g L}^{-1}$  and diuron was not detected at a concentration above 2  $\mu\text{g L}^{-1}$ . It thus appears that small but significant amounts of both atrazine and glyphosate, if not other compounds,

continue to be leached from the railway formation almost 3 months after application and 153 mm of accumulated rainfall.

Significant amounts of atrazine, diuron, oxadiazon and oryzalin were detected in the samples taken from the 'soil' formation beneath the railway ballast.

Maximum detected concentrations ranged from 340  $\mu\text{g kg}^{-1}$  for atrazine to 20  $\mu\text{g kg}^{-1}$  for oryzalin. The detected amounts did not appear to change significantly over a period of 50 days between sampling adjacent to the middle and lower trenches and sampling adjacent to the upper trench. Although it must be borne in mind that the sampling locations were different.

Statistical analysis to examine potential relationships between herbicide physico-chemical properties and losses from the railway formation is difficult because of the lack of sufficient data. However, simple correlation and linear regression analysis suggest that the only physico-chemical parameter that may have influenced losses of herbicide from the railway formation is Koc although the relationship is a weak one and is probably modified by the mass applied.

Two main conclusions can be drawn from these results:

- Although significant amounts of applied herbicides were washed through the railway formation into adjacent drainage ditches, for all compounds except atrazine, both concentrations and estimated losses are at least an order of magnitude less than are those from the roadside study. Patterns of herbicide loss measured in this study are also significantly different from those measured in the roadside study.
- The measured patterns of losses from this study, together with the limited statistical analysis of the relationship between losses and compound physico-chemical properties, suggest that the main dissipation mechanism for herbicides leaching through railway formations is that of adsorption to fine mineral and/or organic material in the ballast and/or underlying 'soil' formations. Microbial degradation does not appear to be a significant contributor to dissipation.

This pilot study has provided some valuable information on the fate of herbicides applied to railway track formations. However, because of the unrealistic application method used and the relative insensitivity of the analytical and sampling techniques, it is recommended that:

- A larger scale field study is conducted using more sensitive analytical techniques, a working railway track, and normal spray practice.
- A laboratory method for carrying out partitioning studies using real railway ballast materials should be developed and applied to a range of compounds including all those used in the study reported here.
- A laboratory method for quantifying degradation of compounds within real railway ballast materials should be developed and applied to a range of compounds including all those used in the study reported here.

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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.

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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 desk study carried out to review the 'state of the art' with respect to herbicide applied to hard surfaces (Heather, 1997), identified two main situations in which where non-agricultural herbicides are used: kerb edges of roads and pavements; railway track formations.

In order to gather preliminary data on the extent to which herbicides may be washed through railway track formations, a pilot study has been carried out on a former test track near Hilton, Derby. This study complements a previous pilot study that investigated the extent to which herbicides applied along a kerb edge adjacent to an asphalt trunk road are washed into receiving drainage gully pots (Heather et al, 1998).

The aim of this railway study is to provide data on herbicide concentrations leaching from a real railway track-bed, for use in the construction of a simple exposure model for a railway scenario.

The main objectives of the study were to:

- Monitor the concentrations of six herbicides leaching from a real railway track bed to surface drains adjacent to the track,
- Monitor concentrations in the 'soil' formation directly beneath the railway ballast of the track bed.

This report describes the materials, methodology and results of the study. It uses the results to test two null hypotheses:

1. Herbicides applied to rail ballast will not be washed to a surface drain during the first 50 mm of rain after herbicide application,
2. Herbicides applied to railway ballast will not leach to a depth of 600 mm in the underlying 'soil' formation following the first 50 mm of rain after herbicide application.

Finally it makes recommendations for further studies to be carried out within the wider consortium project.

## 2 Materials and methods

### 2.1 Study site

A site was selected on the former test track at Hilton, Derby, and a lease negotiated with the managers, Rail Property Ltd. The track bed was constructed for a double railway track but latterly had been used as a single-track test line. All rail tracks had been removed and only the ballast for the single track was still in place. A 50 m section on a slight gradient in a shallow cutting was selected for the study, having ballast in good condition and being well away from housing and so unlikely to be vandalised. The national grid reference of the site was SK26303020.

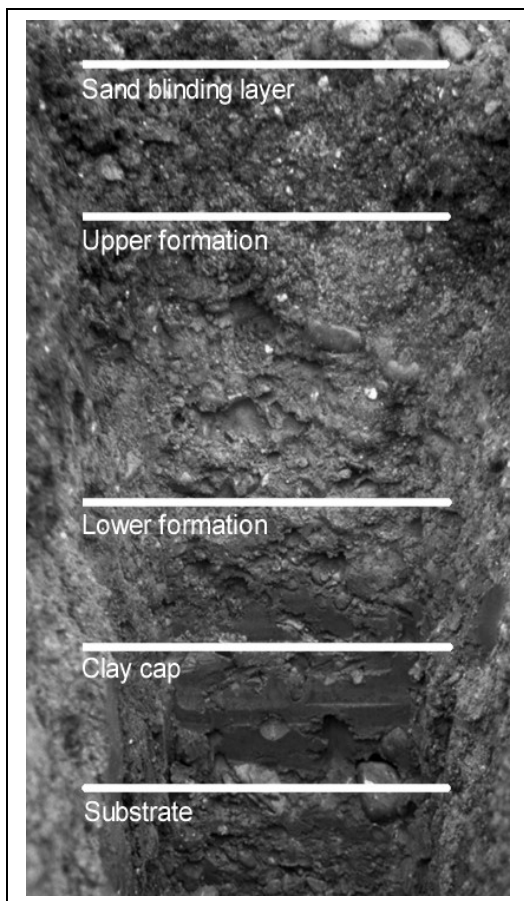


Plate 1: Profile through the railway formation below the two ballast layers. The material shown above the blinding layer is debris from digging the profile.

An area of track below the level of the test site, where a small area of ballast had been removed, was chosen for a preliminary examination and a 300 mm wide profile, dug through the formation (Plate 1) showed the following sequence:

Beneath the two ballast layers (approximately 250 mm of granite ballast on 200 mm limestone ballast) was a 100 mm thick layer of fine 'blinding' material, including sand, ash and stones of less than 5 mm diameter. Below this was a 400 mm thick formation of sandy material and hard core, which included large cobbles and broken bricks. The lower part of this layer contained larger stones than the upper part and passed abruptly into an engineered clay layer 150 mm thick. The underlying substrate material was contaminated with clay in its upper parts but otherwise contained large stones and local sandstone.

When the pit was re-filled the engineered clay material was returned to the original part of the profile to maintain the integrity of the cap.



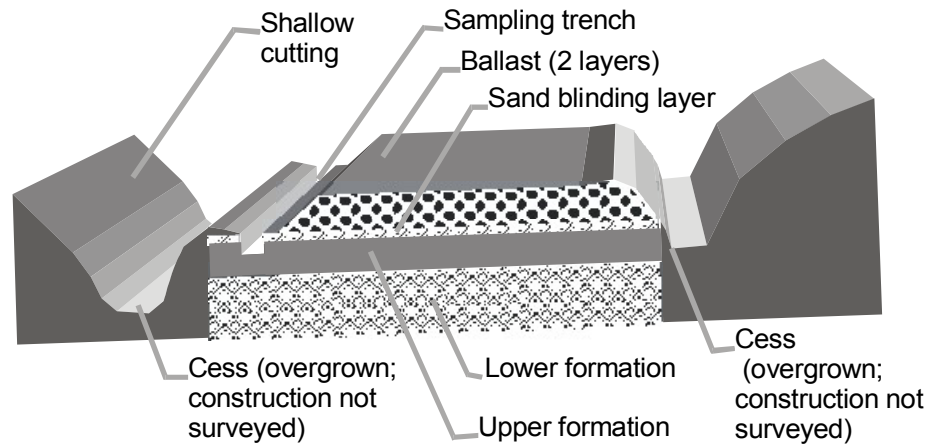


Figure 1: Scheme showing a cross-section of the study site (not to scale), facing up the gradient with the camber sloping down to the left of the figure.

Figure 1 shows a schematic section through the study site, showing how the formation was bordered by an open drain ('cess') on each side, with the cess on the lower side of the camber being the largest. The site had not been used for at least three years and there was more weed growth on the ballast than would normally be expected. A gas burner was used to remove the weed growth from the test site, some two weeks before herbicide application (Plate 2). By the time herbicides were applied the weeds had begun to grow back, with vigorous tillering of grass weeds.



Plate 2: Gas burner used to clear the site prior to the study



Plate 3: One of the sampling trenches, viewed from the ballast side

The cess was so overgrown with weeds that water flow to it was severely restricted. In order to facilitate sampling drainage waters, three trenches were dug through the remaining ballast and blinding layer into the upper formation at the cess side of the single-track bed (Plate 3). These trenches collected through-flow water and divided the test site into three blocks, referred to as 'upper', 'middle' and 'lower' according to their location on the gradient. Each trench was approximately 14 m long, 0.30 m wide and 0.45 m deep, the three being dug in line with a 4 m gap between each (Figure 2).

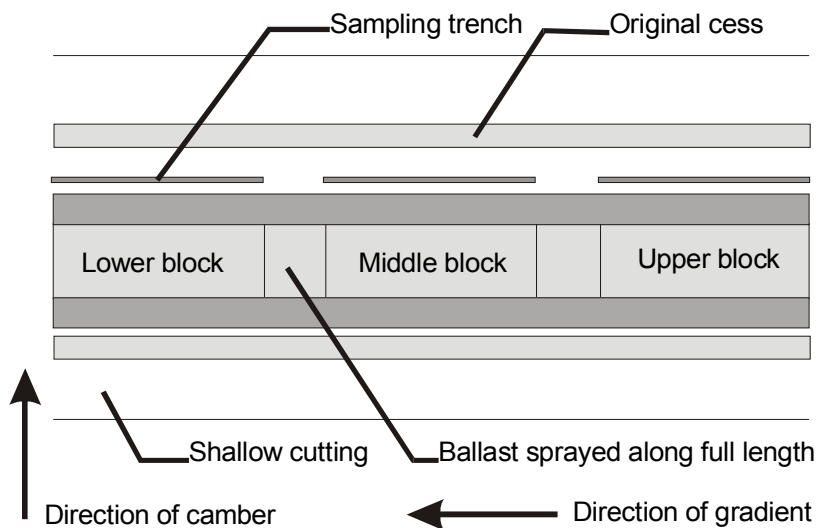


Figure 2: Scheme showing the layout of the study site

The formation in which the trenches were located was sufficiently compact to retain water for a few days after rainfall. This was demonstrated by a test hole of approximately 0.25 m x 0.25 m x 0.3 m deep, dug in an adjacent part of the site

two weeks prior to herbicide application. The trenches were dug on 03 June and immediately collected water from the previous day's rain. This water was removed prior to herbicide application on 04 June 1998.

## 2.2 Selection of test compounds

The selected test compounds were those used in previous studies within the 'hard surfaces' group of projects, thus enabling a direct comparison with their results.

The six test compounds were originally nominated by the 'hard surfaces' project steering group and selected to give a range of physico-chemical properties, mode of action and application rates. Experimental permits had been obtained for compounds not currently registered for non-crop use. Details of the compounds and their properties are given in Table 1 and Table 2.

Table 1: Test compounds selected for the study

Compound	Product	MAFF number	Formulation g.L <sup>-1</sup> AS; type	Application rate g.ha <sup>-1</sup> product	Application rate g.ha <sup>-1</sup> AS
Glyphosate	Roundup Pro Biactive	04146	360; SL	8000	2880
Diuron	Freeway	06047	500; SC	9000	4500
Atrazine	MSS Atrazine 50 FL	01398	500; SC	12000	6000
Oxadiazon	EXP30680B	-	300; WP	15000	4500
Oryzalin	Surflan	-	480; SC	3600	1728
Isoxaben	Flexidor	05104	125; SC	600	75

Key to formulation types: SL: Soluble concentrate, SC: Suspension concentrate, WP: Wettable powder

Table 2: Physico-chemical properties of the test compounds

Compound	K <sub>OC</sub>	Soil DT <sub>50</sub> Days	Solubility in water mg.L <sup>-1</sup>	Photolysis DT <sub>50</sub>
Glyphosate	10000*	47	11600	-
Diuron	480	90 - 180	36.4	-
Atrazine	100	35 - 50	33	-
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<sub>OC</sub> of glyphosate has been measured at between 886 and 60000 for a range of soils

## 2.3 Application of test compounds

Herbicides were applied on 04 June 1998 in good weather with little wind at the study site. The sampling trenches were bailed out prior to herbicide application so

that there was no risk of contaminating the trenches from footwear after herbicide application.

Each herbicide was applied separately, because the compatibility for mixing the formulations was not known. The required amount of each compound was weighed into a measuring cylinder and mixed with the appropriate amount of water for spraying. The spray solutions were placed in labelled high-density polyethylene bottles in a dark box for transport to the test site.

A 'Vermorel 2000 HP' 20 L knapsack sprayer was used for application, because its piston sprayer design is better able to empty the spray tank than a diaphragm sprayer, an important factor since small quantities of spray mix were being applied and any left in the tank could significantly reduce the amount applied. The sprayer was fitted with a Lurmark AN1.2 90° flat fan nozzle and calibrated prior to herbicide application to give a 1 m wide swath when held at the correct height. Each compound was sprayed onto a 250 m<sup>2</sup> area of track in five adjoining swaths along a 50 m length of track.

Approximately 125 mL water was sprayed through the sprayer onto a separate part of the track bed, down gradient from the study site, between the application of each compound, in order to clean the pump and spray line. Plate 4 shows the application method and Table 3 the quantities of active substance and water applied. Approximately ten minutes drying time was allowed between the application of each herbicide, so that the ballast surfaces did not become excessively wet.



Plate 4: Applying a test compound

Table 3: Quantities of active substance and water volumes applied

Compound	Active substance g	Water volume L
Glyphosate	72	6.25
Diuron	112.5	11.25
Atrazine	150	6.25
Oxadiazon	112.5	6.25
Oryzalin	43.25	6.25
Isoxaben	1.88	6.25

## 2.4 Sampling

### 2.4.1 Control water

On 19 May 1998 a small hole, approximately 250 mm square and 300 mm deep, was dug through the ballast and into the upper 'soil' formation. Approximately two weeks later, on 03 June 1998 (the day before herbicide application) the water that had collected in this hole was sampled in two 500 mL HDPE bottles. The sample of control water was split into three sub-samples (one for each analytical laboratory) and then frozen for storage and despatch. The hole was filled in immediately after the control water sample was taken and prior to excavation of the three main sampling trenches (see section 2.1, page 4).

### 2.4.2 Surface water

Water samples were collected from each sampling trench on 08, 10, 11, 15, 16, 18, 22 and 29 June and 03 July 1998. On each occasion samples were taken by submerging HDPE bottles in each trench, taking care not to disturb any sediment on the bottom of the trench. Three 250 mL bottles were filled from each trench and after all three trenches had been sampled, they were bailed by hand using a 10 L bucket, the water being tipped into the cess. The trenches were bailed as dry as practicable, so that they would be reasonably dry for the next rainfall event.

On 07 July 1998, following destructive sampling of the 'soil' formation below the ballast (see section ??), the middle and lower trenches were filled in and subsequent samples, taken on 27 July and 24 August 1998, were obtained from the upper trench only.

### 2.4.3 Formation material

Samples of the 'soil' formation beneath the railway ballast were taken in three sampling blocks, one adjacent to each of the water sampling trenches. Samples adjacent to the lower and middle trenches were taken on 07 July. By this date 67.5 mm of rain had fallen since application of the compounds. Samples adjacent to the upper trench were taken on 26 August by which date 134 mm of rain had fallen since application.

Within each sampling block, five small pits were dug using a mechanical excavator. Each pit was dug through the ballast and 'soil' formation to the top of the underlying clay cap. The soil formation along one side of each pit was then carefully picked back to expose fresh soil formation uncontaminated by residue from the digger bucket. Samples were then excavated from the freshly exposed side of the pit, well above any excavation spoil remaining at the base of the pit. In this way the risk of sample contamination was minimised. Within each pit, sample material was taken from two separate points. Each of the two sets of samples from each of the five pits was placed into three doubled LDPE polythene bags to give three replicates each of ten sub-samples of soil formation representative of each sampling block. The 30 replicate bags each contained a minimum of 2.5kg of sampled material.

The samples were stored frozen until all three blocks had been sampled. The material was then defrosted at room temperature and screened through a 5.60 mm wire mesh sieve, removing large stones from the samples and reducing considerably their size and weight. The separated stones were moist and retained some fine earth material on their surfaces. Nevertheless they were discarded without further treatment because washing could have removed any herbicide residues within the fine earth material. At this stage the decision was taken to carry out only one set of analysis from each block and so all the replicates were bulked to give one large sample. A sub-sample of the bulked material from the upper and middle trenches was taken and the moisture content of the sieved material measured by oven drying (Table 4). The bulked samples were then re-frozen ready for despatch for analysis.



Plate 5: Sampling the lower formation

Table 4: Moisture content of the sieved formation material

	Sample adjacent to the middle trench (sampled 07 July)	Sample adjacent to the upper trench (sampled 26 Aug)
Mass wet (g)	112.30	99.17
Mass dry (g)	100.14	89.48
Moisture (g)	12.16	9.69
Moisture %	10.83	9.77

## 2.5 Analysis

Surface water and ‘soil’ formation samples were sent to analytical laboratories in insulated containers with ice packs to keep them frozen. Different laboratories were used for different compounds, depending upon sponsorship and analytical capability (Table 5). Herbicide concentrations were determined by documented methods developed by the individual laboratories.

Table 5: Analytical laboratories used and limits of detection for the water samples

Compound	Laboratory	Lower validation limit (LVL) $\mu\text{g.L}^{-1}$
Glyphosate	Huntingdon Life Sciences, Eye UK	0.05
Diuron	Rhône-Poulenc, Ongar UK	10
Atrazine	Rhône-Poulenc, Ongar UK	10
Oxadiazon	Rhône-Poulenc, Ongar UK	20
Oryzalin	Dow AgroSciences, Wantage UK	10
Isoxaben	Dow AgroSciences, Wantage UK	10

Analytical detections between the lower validation limit (LVL) and 20 % of the LVL could not be quantified and are always reported as ‘<LVL’. Concentrations below 20 % of the LVL could not be detected by the analytical procedures and corresponding values are reported as ‘not detected’ (ND).

## 2.6 Rainfall measurement

Rainfall was measured by a tipping bucket rain gauge and a data logger installed at Barrow-upon-Trent, 7 km from the study site (SK33282870). Rainfall was recorded at hourly intervals and summarised to give daily totals and accumulated rainfall for the study, relative to the day of herbicide application (day 0). This data was used because equipment installed at a farm adjacent to the study site failed and the nearest SSLRC study site to the railway study was Barrow-upon-Trent, no other local sources of data being available.

## 3 Results

### 3.1 Rainfall

Daily rainfall is shown in Figure 3, relative to the day of herbicide application (day 0). Although there was no rainfall on the day of application, unusually large rainfall events occurred on the two days prior to application and resulted in considerable flow into the sampling trenches, which needed to be bailed out before the herbicides were applied (see section ??, page 4).

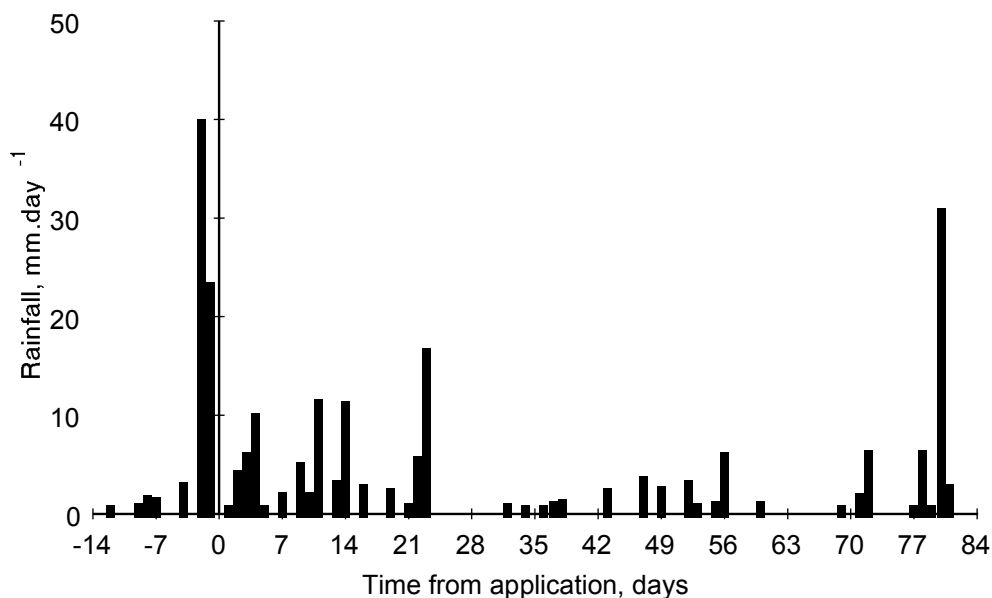


Figure 3: Daily rainfall at Barrow-upon-Trent

Figure 4 shows the accumulated rainfall following herbicide application, in relation to the surface water sampling dates. Rainfall subsequent to application on 04 June was unusually large for the time of year and when the penultimate water sample was taken on 29 June, only 25 days after application, 81.8 mm of rain had fallen on the site. Individual rainfall events of 10 mm or more occurred on 08, 15, 18 and 27 June and a very large event of 30 mm occurred on 23 August, the day before the final water sample was taken from the upper trench.



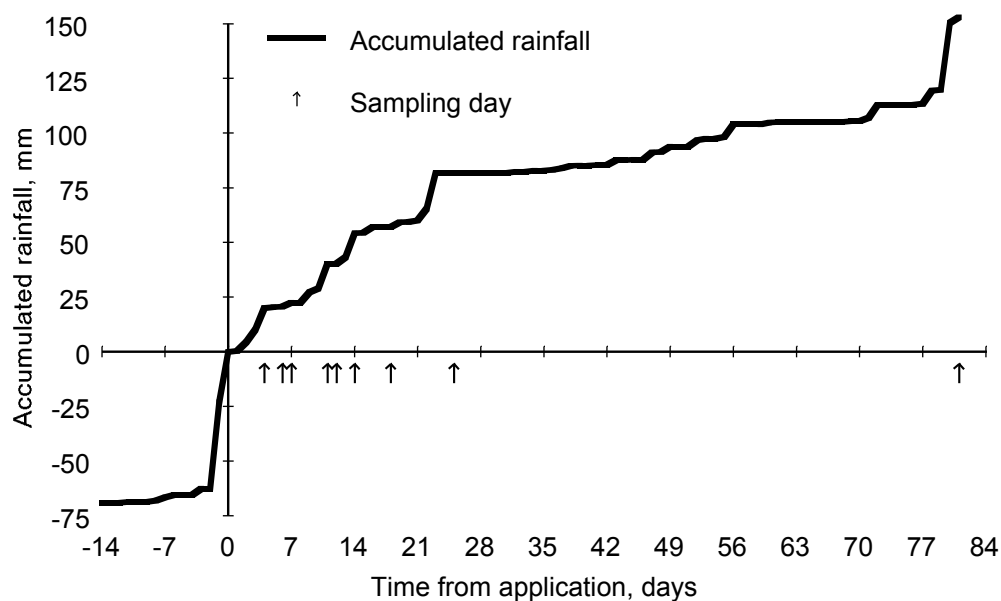


Figure 4: Accumulated daily rainfall and sampling days

## 3.2 Herbicide concentrations

### 3.2.1 In control water

Results of the control water sample analyses are given in Table 6. Neither diuron nor atrazine were detected (above  $2 \mu\text{g L}^{-1}$ ) in the control water sample. Glyphosate, oxadiazon and isoxaben appeared to give positive detections but not at quantifiable levels, whereas oryzalin appeared to be detected at the lower validation level.

It is unlikely that any of the compounds that appeared to be detected at or below LVL were present in the water, since the railway had not been used for several years. Two of the compounds most likely to have been used at some time in the past (atrazine and diuron) were not detected. Glyphosate might also have been used to treat the railway, but is unlikely to have persisted for such a long time. It is possible that there has been more recent use of glyphosate by neighbouring landowners but there was no evidence of weed control in the vicinity of the track and the adjoining land was all under grass.

The apparent presence of small, unquantifiable herbicide residues in the control water might be explained by the presence of other organic contaminants, possibly oil of fuel residues from the track bed, which might have interfered with the analytical methodology. The possible presence of such contaminants needs to be taken into account when discussing the analytical results from the surface water samples. Quantitative concentrations well in excess of the LVL are unlikely to be incorrect but those at or near the LVL could well reflect the presence of unknown organic contaminants and should be treated with caution.

Table 6: Control water sample results

Compound	Concentration $\mu\text{g L}^{-1}$
Glyphosate	<0.05
Diuron	ND
Atrazine	ND
Oxadiazon	<20
Oryzalin	10
Isoxaben	<10

### 3.2.2 In surface water

Measured concentrations for all the compounds are given in appendix 8.2.1 and results for those compounds with significant detections are shown graphically in Figures 5, and 6. For illustrative purposes, concentrations reported by the analysts as '< LVL' are shown on the graphs as one fifth of the LVL value, to differentiate them from 'not detected' results which are shown as 0.

Of the six herbicides analysed, glyphosate, diuron and atrazine gave significant quantifiable detections whereas the other three, oxadiazon, oryzalin and isoxaben gave uncertain or negative detections. It should be noted however that the LVL for glyphosate is approximately 200 times lower than that for the other compounds studied. If the LVL for glyphosate had been similar to that of the other compounds, its pattern of detection would have been similar to that of oxadiazon, oryzalin and isoxaben.

Although **oxadiazon**, **oryzalin** and **isoxaben** all appeared to give some detections at or below the LVL, these compounds also gave similar detections for the control water samples. It is thus uncertain whether the apparent detection of the three compounds in the drainage ditch samples represents a real detection or a similar false detection to that attributed to the control water samples.

For all three compounds that were detected at concentrations significantly greater than the LVL (**glyphosate**, **diuron** and **atrazine**), maximum concentrations from all three sampling trenches always occurred in the second sample, taken on 10 June. This peak appears to be the result of the significant rainfall events on the 07 and 08 June, three to four days after application, although the drainage water samples taken on the 08 June, in response to these events, do not show such large concentrations. Subsequent sampling showed other smaller concentration peaks on some occasions in most drainage ditches, but the pattern is not consistent for all compounds. Detailed individual patterns are described below. On the last sampling occasion, 81 days after application, when only the upper trench was sampled, glyphosate was detected at a concentration of  $0.8 \mu\text{g L}^{-1}$ , atrazine was detected at the LVL concentration of  $10 \mu\text{g L}^{-1}$  and diuron was not detected at a concentration above  $2 \mu\text{g L}^{-1}$ .

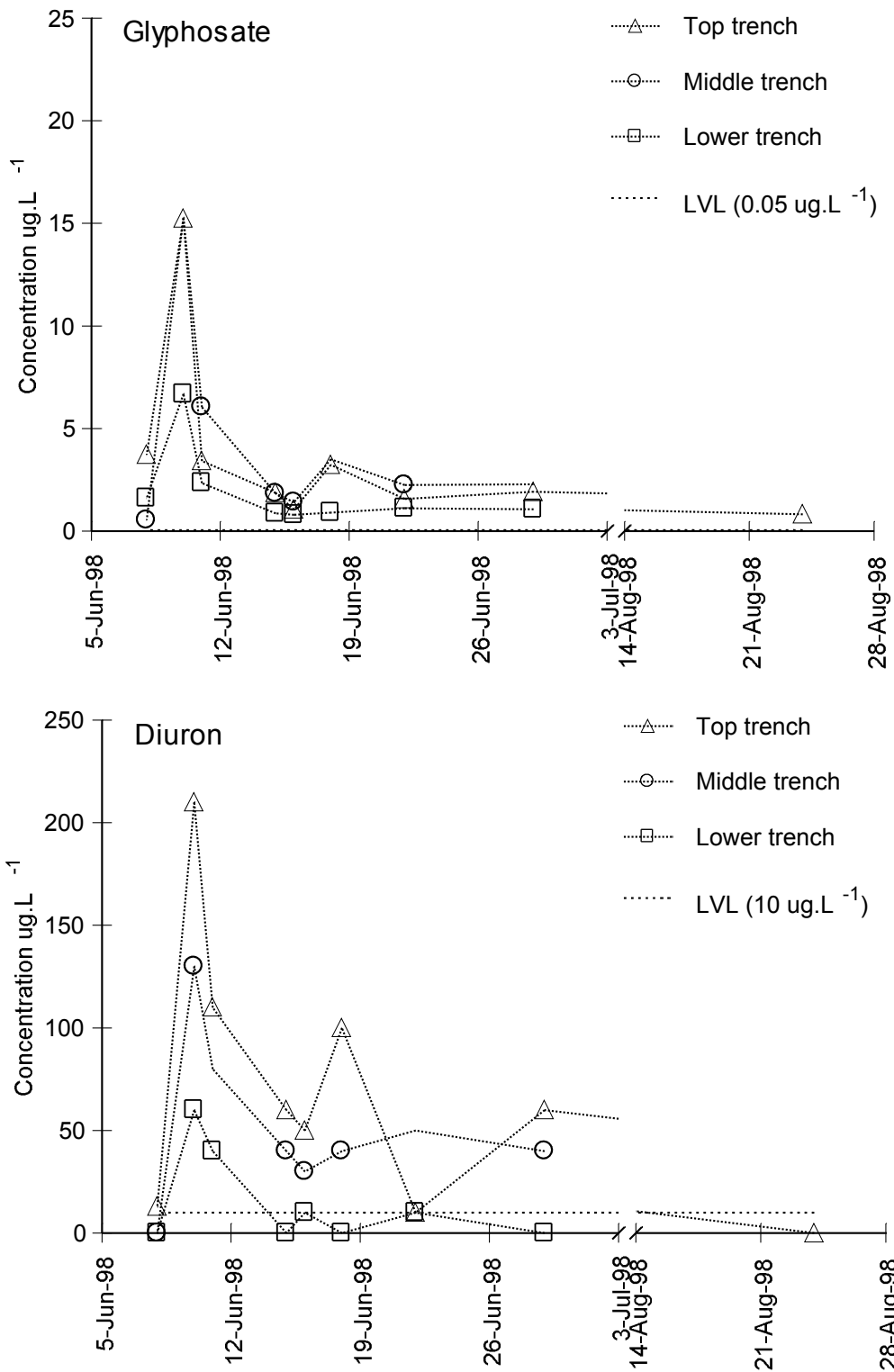


Figure 5: Concentrations of glyphosate and diuron in water samples taken from three trenches in a railway track

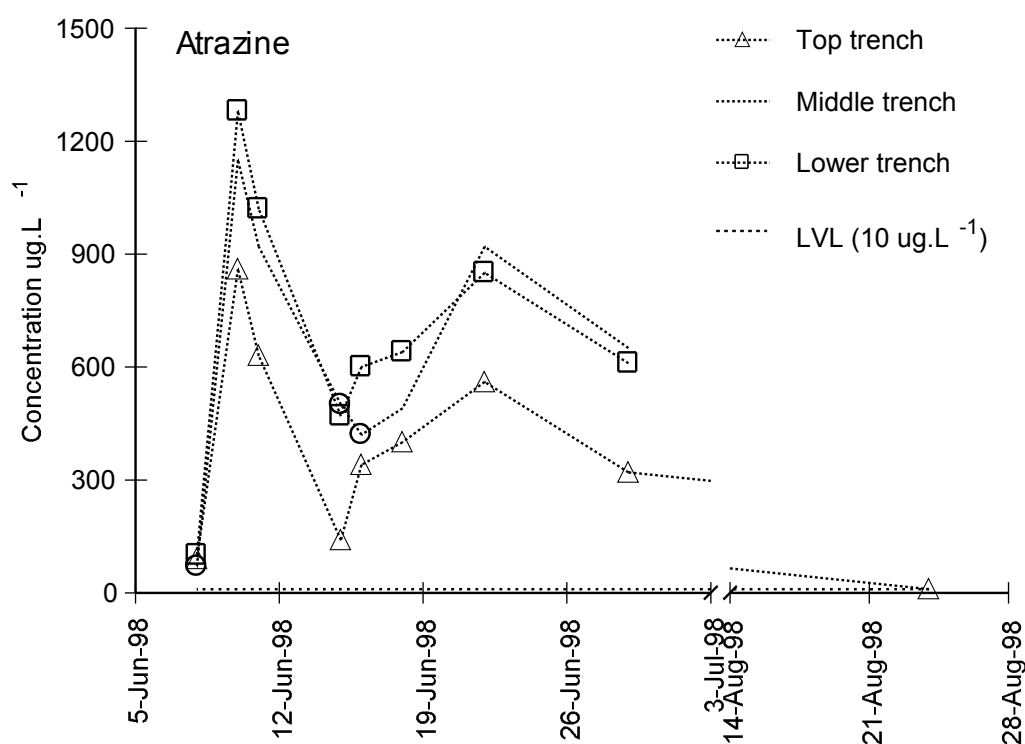


Figure 6: Concentrations of atrazine in water samples taken from three trenches in a railway track

For **glyphosate**, concentrations in the upper and middle trenches were very similar on all sampling occasions. A maximum concentration of  $15 \mu\text{g L}^{-1}$  was detected in the second sample (taken 6 days after application) and a further, much smaller 'peak' of  $3.2$  to  $3.5 \mu\text{g L}^{-1}$  was present in the sixth sample (taken 14 days after application). Concentrations of samples taken from the lower trench were much smaller than those from the upper and middle trenches and do not show a second 'peak'.

Concentrations of **diuron** show a similar pattern to those of glyphosate for the first four sets of samples taken (4, 6, 7 and 11 days after application) although the values are an order of magnitude greater with a maximum concentration of  $210 \mu\text{g L}^{-1}$  present in the second sample taken from the upper trench. However there appears to be a consistent decline in concentrations from the upper to the lower trenches with maximum concentration in the lower trench less than one third that of the upper trench. In the lower trench, concentrations of the fifth and all subsequent samples are at or below the LVL ( $10 \mu\text{g L}^{-1}$ ). Two secondary 'peaks' in diuron concentrations appear to be present in the sixth and eighth samples taken from the upper trench, 14 and 25 days after application. These peaks are not apparent in samples taken from the middle trench, which show only small increases and decreases in concentration over the four sampling occasions between 11 and 25 days after application.

**Atrazine** concentrations were the largest of all three detected compounds with a maximum of 1280  $\mu\text{g L}^{-1}$  present in the second sample taken from the lower trench (6 days after application). In contrast to both diuron and glyphosate, the smallest concentrations of atrazine were detected in the upper trench. All three trenches show a secondary peak concentration of between 560 and 920  $\mu\text{g L}^{-1}$  in the seventh sample to be taken (18 days after application). In the upper and lower trenches atrazine concentrations show a steady increase from the fourth to the seventh samples, taken 11, 12, 14 and 18 days after application, and then decline in the final two samples, taken 25 and 81 days after application. In the middle trench however, concentrations continue to decline between the fourth and fifth sample and do not increase until the sixth sample, taken 14 days after application.

### 3.2.3 In the formation material

Concentrations measured in samples taken from the 'soil' formation material are given in Appendix 8.2.2 and shown graphically in figure 8. Isoxaben was not analysed in any of the samples taken.

Glyphosate was not detected in any of the samples but significant concentrations of diuron, atrazine and oxadiazon were detected in the bulked samples from all three blocks. Detections of oryzalin in the samples were equivocal. On 03 July, 29 days after application, the compound was detected at a concentration of 20  $\mu\text{g kg}^{-1}$  in samples taken from the lower block whereas samples from the middle block gave an apparent positive but unquantifiable detection below the LVL. The third sample, taken from the upper block on day 26 August, 84 days after application, appeared to contain oryzalin at the LVL of 10  $\mu\text{g kg}^{-1}$ . In view of the possible interference of unknown organic contaminants with the analysis (see section 3.2.1), apparent positive oryzalin detections at or around the LVL of 10  $\mu\text{g kg}^{-1}$  are questionable.

The greatest concentrations of both diuron and atrazine (220 and 340  $\mu\text{g kg}^{-1}$  respectively) were detected in material from the lower block (sampled 29 days after application). In contrast, the greatest concentration of oxadiazon was detected in material taken from the upper block (sampled 84 days after application), although it only differs by 20  $\mu\text{g kg}^{-1}$  from that of the lower block. For all the detected compounds, concentrations appear to decline between the lower and middle sampling blocks. Comparison of concentrations from these blocks with those from the upper sampling block is unlikely to be valid because of the long time difference between their sampling dates.

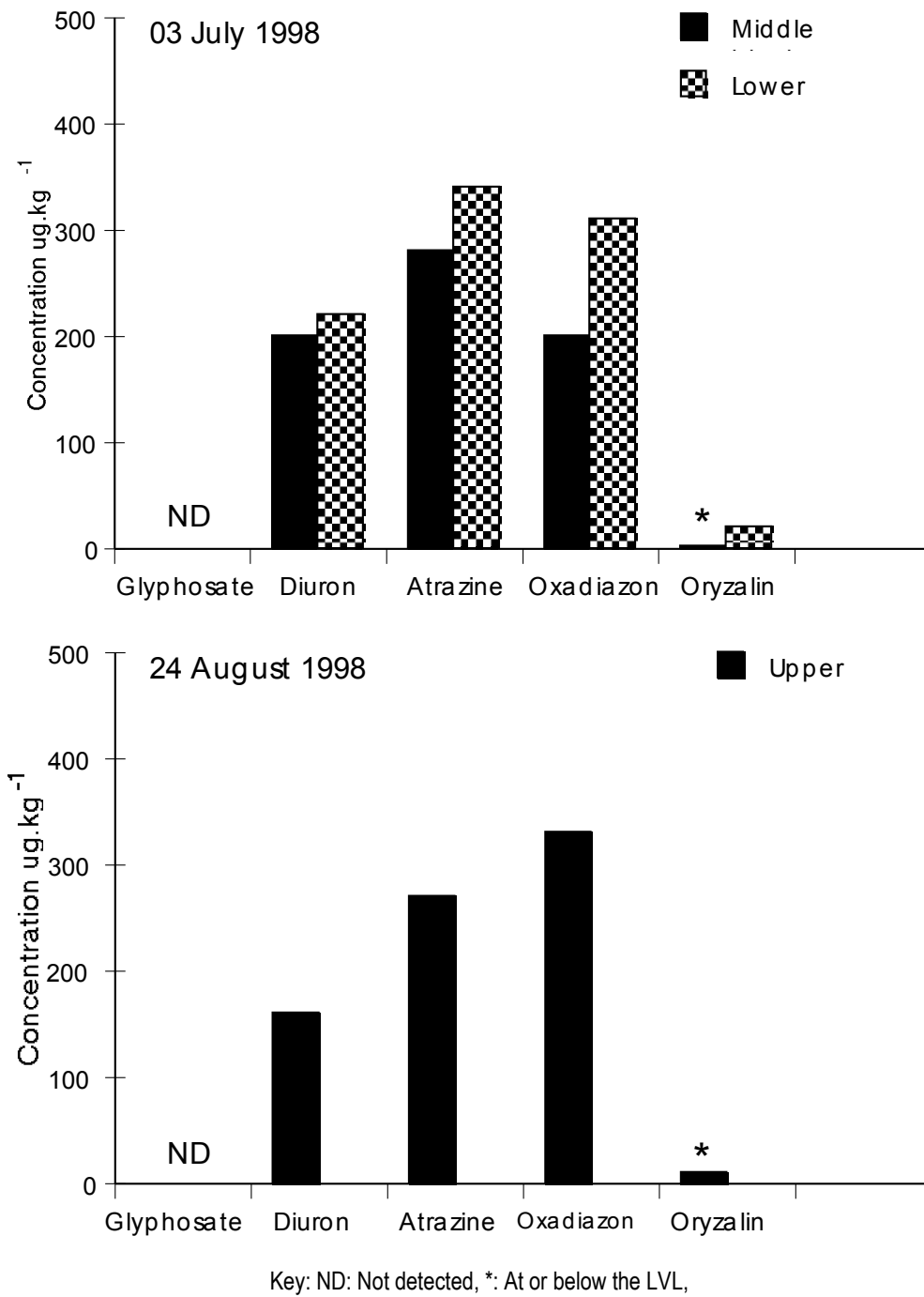


Figure 7: Concentrations in the formation samples taken from the lower formation (isoxaben was not analysed)

## 4 Data analysis and discussion

### 4.1 Comparison with the results of the roadside pilot study

#### 4.1.1 Maximum measured concentrations

Maximum measured concentrations of the six compounds applied in the railway site are compared with maximum measured concentrations of the same compounds from the Roadside study in Table 7. For all compounds except isoxaben, maximum concentrations from the railway are considerably less than those from the roadside. For isoxaben, no meaningful comparison could be made as the maximum concentrations detected in both studies were less than the LVL. For those compounds where quantitative comparisons can be made, the ratios of railway : roadside concentrations are almost 0.5 for atrazine, 0.07 for diuron and 0.02 for glyphosate.

Table 7: Maximum measured concentrations ( $\mu\text{g L}^{-1}$ ) of detected herbicides measured in drainage samples from the railway and roadside studies.

	Glyphosate	Diuron	Atrazine	Oxadiazon	Oryzalin	Isoxaben
Roadside study	650	1810	2250	390	70	<10
Railway study	12.4	133	1097	<20	<10	<10
Railway/Roadside	0.019	0.073	0.49	N.A.	N.A.	N.A.

However, such a straight comparison of maximum measured concentrations does not take into account differences in the amount of compound applied in the two studies. A further comparison was therefore carried out using the maximum concentrations detected relative to the amount of active ingredient applied, as a simple way to standardise the results. Table 8 shows the maximum concentrations of quantifiable detected compounds in the roadside and railway pilot studies, expressed relative to the amount of active substance applied in each study. It can be seen that when standardised in this way, the relative maximum concentrations are even higher from the roadside in comparison to the railway.

Table 8: Maximum concentration of detected compounds relative to the amount of active substance applied, for the roadside and railway pilot studies.

Compound	Amount applied g AS		Maximum concentration $\mu\text{g.L}^{-1}$		Relative detection $\mu\text{g.L}^{-1}.\text{g}^{-1}$ AS	
	Road	Railway	Road	Railway	Road	Railway
Glyphosate	0.86	72	650	12.4	755.8	0.1722
Diuron	1.30	112.5	1810	133	1392	1.182
Atrazine	1.44	150	2210	1097	1535	7.313

#### 4.1.2 Estimated accumulated percentage losses

Accurate calculation of accumulated % losses from the railway study is not possible because drainage flows could not be measured. However an approximate calculation can be made based on the following assumptions:

- The total volume of rain falling on the area of the experimental site all drains through the sample trench area at the side of the track. (This is very likely to over-estimate the actual drainage as it takes no account of evapotranspiration losses or water retention within the railway formation).
- The experimental area of track that was sprayed is 250 sq m. (5m wide by 50 m long). The area containing the sampling trenches adjacent to the experimental site is 65 sq. m. (1.3m wide and 50 m long). The total area draining to the sampling trench is therefore 315 sq m.
- The average of the three concentrations measured in samples taken from the three trenches represents the average drainage concentration in all drainage waters from the sprayed area.
- For any specific sampling event, the mean of the average concentration of samples for that event and the previous one represents the average concentration of the total accumulated drainage between the sampling events.

Calculations of approximate percentage losses for the railway study using this methodology are given in Table 9 and comparisons of these estimated losses with the measured accumulated percentage loss of the same compounds for the first treatment of the roadside study are shown in Figure 8. It is appropriate to compare losses from the railway study with those from the roadside study first treatment because in both studies, significant rainfall occurred in the days immediately after herbicide application and sampling had virtually been completed by 25 days after application. It should be remembered however that by 25 days after application, there had been 81.8 mm of accumulated rainfall in the railway study but only 25.4 mm in the roadside study.

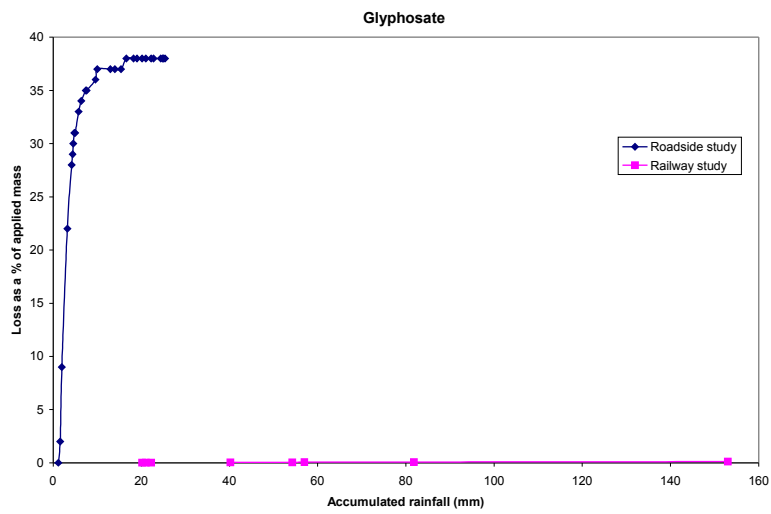
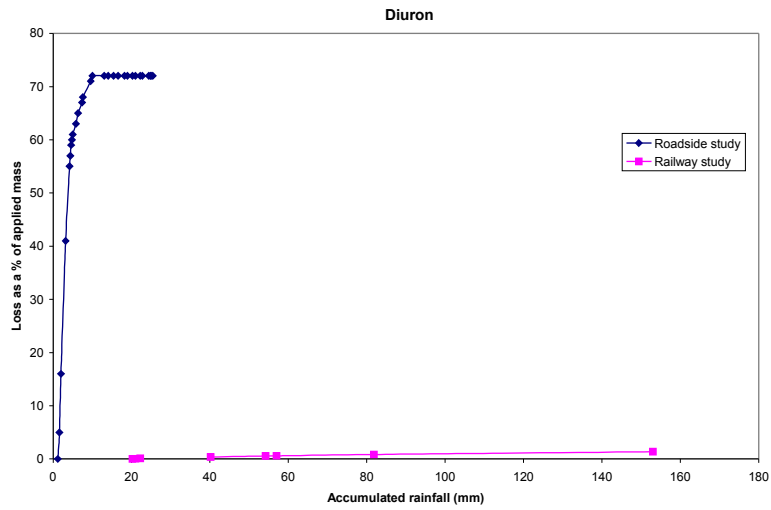
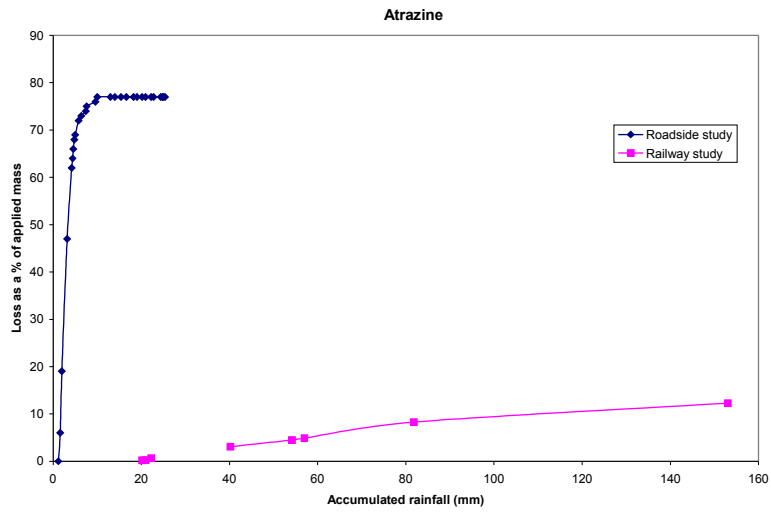
Three main conclusions can be drawn from the comparisons shown in figure 8. Firstly, compared to the roadside wash-off patterns, the railway study shows a significant time lag before significant amounts of compound are washed off to the adjacent drainage ditches. Secondly, for equivalent amounts of rainfall, percentage losses from the railway are at least an order of magnitude less than those from the roadside study. Although there is considerable uncertainty attached to the method for estimating percentage losses from the railway study, even if losses were underestimated by 100%, there would still be significantly less compound lost from the railway than from the roadside for equivalent amounts of accumulated rainfall. Finally, it is evident from the analytical data that, at least for glyphosate and atrazine, small but significant losses appeared to be continuing up to 81 days



after application and 154 mm of accumulated rainfall. This contrasts strongly with the Roadside study where losses of compounds appeared to be virtually complete after only 3 days and 10 mm of accumulated rainfall.

Table 9: Estimated accumulated percentage losses of detected herbicides calculated from measured concentrations of samples from the drainage trenches.

Days after application	Accumulated rainfall (mm)	Accumulated drainage between sampling events (L)	Average conc. ( $\mu\text{g L}^{-1}$ ) between sampling events	Accumulated mass (g) lost in drainage	Accumulated % loss of applied mass
<b>Glyphosate</b>					
4	20	6300	1.0	0.006	0.008
6	20.6	189	7.2	0.007	0.010
7	22.4	567	8.2	0.012	0.017
12	40.2	5607	2.6	0.027	0.037
14	54.2	4410	1.8	0.035	0.048
18	57	882	2.1	0.037	0.051
25	81.8	7812	1.7	0.045	0.069
81	153	22428	1.3	0.079	0.109
<b>Diuron</b>					
4	20	6300	6.5	0.041	0.036
6	20.6	189	73.0	0.055	0.049
7	22.4	567	105.0	0.114	0.102
12	40.2	5607	53.5	0.414	0.368
14	54.2	4410	50.0	0.635	0.564
18	57	882	46.5	0.676	0.601
25	81.8	7812	36.5	0.961	0.854
81	153	22428	25.0	1.523	1.354
<b>Atrazine</b>					
4	20	6300	43.5	0.274	0.183
6	20.6	189	592.0	0.386	0.257
7	22.4	567	977.0	0.940	0.627
12	40.2	5607	655.0	4.612	3.075
14	54.2	4410	481.5	6.736	4.491
18	57	882	643.5	7.303	4.869
25	81.8	7812	652.0	12.397	8.265
81	153	22428	268.5	18.419	12.279



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

There are problems when investigating the relationship between wash-off and physico-chemical properties of applied compounds for the railway study. Data related to percentage losses are only estimated and also can only be derived for three of the six compounds. There is more certainty about the values for maximum measured concentrations but again, data is only available for three compounds because of the uncertainty attached to the small unquantifiable apparent detections of oxadiazon, oryzalin and isoxaben (see section 3.2.1). There is thus very little data to undertake any meaningful statistical analysis. Nevertheless, it was decided to investigate the relationship between physico-chemical properties and estimated accumulated percentage losses for the three quantifiable compounds, atrazine, diuron and glyphosate. The relationship between estimated accumulated percentage loss and the Koc, solubility, soil DT50 and mass applied was initially investigated using simple correlation. Because of the large range in values for all parameters used in the analysis, all values were converted to a  $\text{Log}_{10}$  base. Results are shown in Table 10.

**Table 10.** Correlation matrix for  $\text{Log}_{10}$  estimated % loss and  $\text{Log}_{10}$  physico-chemical data for the 3 quantifiable herbicides.

	$\text{Log}_{10}$ mass applied	$\text{Log}_{10}$ Koc	$\text{Log}_{10}$ solubility	$\text{Log}_{10}$ DT50
$\text{Log}_{10}$ % loss	<b>0.9963</b>	<b>-0.9897</b>	<b>-0.8913</b>	-0.0402
$\text{Log}_{10}$ mass applied	<b>1</b>	<b>-0.9983</b>	<b>-0.9268</b>	0.0454
$\text{Log}_{10}$ Koc	<b>-0.9983</b>	<b>1</b>	<b>0.9470</b>	-0.1031
$\text{Log}_{10}$ solubility	<b>-0.9268</b>	<b>0.9470</b>	<b>1</b>	-0.4172
$\text{Log}_{10}$ DT50	0.0454	-0.1031	-0.4172	<b>1</b>

Significant correlations are highlighted in **bold print**

$\text{Log}_{10}$  mass applied,  $\text{Log}_{10}$  Koc and  $\text{Log}_{10}$  solubility are each significantly correlated with the  $\text{Log}_{10}$  percentage loss. However, the correlation matrix shows that  $\text{Log}_{10}$  mass applied is also significantly correlated with  $\text{Log}_{10}$  Koc and  $\text{Log}_{10}$  solubility, each having a correlation coefficient larger than that of  $\text{Log}_{10}$  percentage loss with  $\text{Log}_{10}$  Koc or  $\text{Log}_{10}$  solubility. This apparent strong correlation between the physico-chemical parameters of the herbicides investigated highlights the problem of the very limited dataset available for statistical analysis.

In order to get a better idea of the actual significance of the three parameters that are correlated with percentage loss, a regression analysis was undertaken. Multiple linear regression could not be performed because of the strong interdependence of the three physico-chemical parameters investigated. Results of the three individual linear regression analyses are shown in table 11. They show that none of the individual relationships investigated are significant at a 95%

confidence level, whereas only Log<sub>10</sub> mass applied and Log<sub>10</sub> Koc are significant above a 90% confidence level.

**Table 11.** Linear regression analysis of the effect of individual physico-chemical properties on estimated percentage loss for the 3 quantifiable herbicides.

Independent variable	Adjusted r <sup>2</sup>	relationship	Significance <sup>1</sup>	Confidence level which is significant
Log <sub>10</sub> Mass applied	0.9591	positive	n.s.	94%
Log <sub>10</sub> Koc	0.9854	negative	n.s.	90%
Log <sub>10</sub> solubility	0.5889	negative	n.s.	70%

<sup>1</sup> n.s. Not significant at a 95% confidence level

When interpreting this analysis, it is important to bear in mind the potential relationships with physico-chemical data for the three compounds that did not have quantifiable information on percentage losses. In order to do this, the average concentration of runoff samples was estimated using the methodology outlined in section 4.1.2 above. These values were then compared to predictions of the average concentration of runoff samples using the two ‘best’ individual regression models derived for table 11 (those for mass applied and Koc). The results are shown in table 12.

**Table 12.** Comparison of estimated average concentrations (µg L<sup>-1</sup>) based on measured data and regression models using mass applied and Koc.

	Atrazine	diuron	glyphosate	oxadiazon	oryzalin	isoxabe
Estimated using measured data	382.2	31.6	1.63	<20	<10	<10
Estimated using Koc regression	296.6	46.4	1.43	7.0	9.5	0.3
Estimated using mass applied regression	331.9	39.8	1.49	39.8	0.03	3.2E-12

They suggest that Koc may be a more reliable indicator of losses than the mass applied. This is because the estimated average concentration of oxadiazon using the mass applied regression gives a value of 39.8 µg L<sup>-1</sup>, the same as for diuron, whereas the measured data were never above the LVL of 20 µg L<sup>-1</sup>. For all other compounds, estimates using either regression model give values that do not contrast strongly with estimates from the measured data.

From this very limited analysis, it appears that the only physico-chemical parameter that may have influenced losses of herbicide from the railway formation is Koc although the relationship is a weak one and is probably modified by the mass applied. No significant relationship could be established between estimated percentage loss and solubility. As with the roadside study, the derived correlation is negative and thus the opposite of what would be expected, illustrating the overriding influence of glyphosate with its very large solubility.

### **4.3 Implications of the results for the dissipation of herbicides applied to railways**

The results presented in the previous two sections can only provide some tentative clues with respect to herbicide dissipation. Firstly, the relatively small accumulated percentage losses estimated for those compounds with quantifiable data suggest that there is significant dissipation of herbicides that are applied to railway formations. The obvious lag time to herbicide wash-off (see figure 8), the weak negative relationship of percentage loss with Koc and the presence of significant concentrations of diuron, atrazine, oxadiazon and possibly oryzalin within the 'soil' formation samples taken from below the railway ballast, all suggest that there is significant adsorption to fine mineral and/or organic material in the ballast and underlying 'soil' formations.

In contrast, the lack of any significant relationship between soil DT50 and estimated percentage loss suggests that microbial degradation is not an important contributor to dissipation. This is further implied by the fact that, for all three herbicides with quantifiable concentrations, significant losses of herbicide were still occurring almost 3 months after application and 153 mm of accumulated rainfall.

## 5 Conclusions

The data generated from this study have disproved both null hypotheses postulated at its inception:

- Significant amounts of some, if not all herbicide compounds applied to the railway formation were washed into adjacent surface ditches. Maximum detected concentrations ranged from 1097  $\mu\text{g l}^{-1}$  for atrazine to 12.4  $\mu\text{g l}^{-1}$  for glyphosate with estimated accumulated percentage losses ranging from 12.3 % to 0.1% respectively.
- Significant amounts of most of the applied herbicides were leached up to a depth of 500 mm below the ballast formation. Maximum detected concentrations ranged from 340  $\mu\text{g kg}^{-1}$  for atrazine to 20  $\mu\text{g kg}^{-1}$  for oryzalin.

Further interpretation of the results is limited because of problems with the relatively high analytical validation levels for most of the studied compounds, the possible interference of organic contaminants with compound analysis and the difficulty of deriving reliable estimates of percentage losses. Nevertheless a number of additional conclusions can be drawn.

Firstly, although significant amounts of applied herbicides were washed through the railway formation and into adjacent drainage ditches, both maximum measured concentrations and estimated accumulated potential losses are significantly less than are those from the roadside wash-off study. For all compounds except atrazine, both concentrations and estimated losses are at least an order of magnitude less than are those from the roadside study.

Secondly, the patterns of herbicide loss measured in this study are significantly different from those measured in the roadside wash-off study in that:

- There is a significant time lag before quantifiable amounts of herbicide are washed through the railway formation into the adjacent drainage ditches.
- Small but significant amounts of some if not all, herbicides continue to be lost into the drainage ditches up to 81 days after application and 154 mm of accumulated rainfall.

In addition, the amounts of herbicide detected in the 'soil' formation below the railway ballast do not appear to change significantly over a period of 50 days between sampling adjacent to the middle and lower trenches and sampling adjacent to the upper trench. Although it must be borne in mind that the sampling locations were different.

Finally, the measured patterns of losses from this study, together with the limited statistical analysis of the relationship between losses and compound physico-chemical properties, suggest that the main dissipation mechanism for herbicides leaching through railway formations is that of adsorption to fine mineral and/or organic material in the ballast and underlying 'soil' formations. Microbial degradation does not appear to be a significant contributor to dissipation.

## 6 Recommendations

This pilot study has provided quantitative evidence for the movement of herbicides applied to railway formations into non-target surface water bodies and underlying soil and substrate materials. It has also suggested some potential dissipation mechanisms for herbicides applied in such environments. However, limitations arising from the unrealistic application method used and the relative insensitivity of the analytical and sampling techniques, mean that further studies are needed to clarify a number of the issues raised. It is therefore recommended that:

- A larger scale field study is conducted using a working railway track, normal spray practice, emulating real-life conditions as far as possible. The study should focus on monitoring movement to groundwater as well as to adjacent surface waters and should, if possible, sample leachate waters moving through the soil/substrate material underlying the railway ballast formations. The study should also use more sensitive analytical techniques that allow the quantification of very small residues down to quantities of at least  $0.1 \mu\text{g l}^{-1}$ .
- A laboratory method for carrying out partitioning studies using real railway ballast materials should be developed. The method should be used to quantify the partitioning and adsorption / desorption potential of a range of compounds including all those used in the study reported here.
- A laboratory method for quantifying degradation of compounds within real railway ballast materials should be developed. The method should be used to quantify degradation rates of a range of compounds including all those used in the study reported here.

## **7 References**

- Heather A. I. J. (1997). Herbicide losses from hard surfaces: Desk study report. Report to 'Hard surfaces' steering committee by Soil Survey and Land Research Centre, Cranfield University. February 1998, 40 pp.
- Heather A I J, Shepherd A J and Hollis J M (1998): Losses of six herbicides from a kerb and gully-pot road drain. Report to 'Hard surfaces' steering committee by Soil Survey and Land Research Centre, Cranfield University. December, 1998, 28pp.



## 8 Appendix: data tables

### 8.1 Daily rainfall at Barrow-upon-Trent

Date	Days after spraying	Rainfall mm	Date	Days after spraying	Rainfall mm
21 May 1998	-14	-	10 Jul 1998	36	0.4
22 May 1998	-13	-	11 Jul 1998	37	0.8
23 May 1998	-12	0.4	12 Jul 1998	38	1
24 May 1998	-11	-	13 Jul 1998	39	0.2
25 May 1998	-10	-	14 Jul 1998	40	-
26 May 1998	-9	0.6	15 Jul 1998	41	0.2
27 May 1998	-8	1.4	16 Jul 1998	42	-
28 May 1998	-7	1.2	17 Jul 1998	43	2.2
29 May 1998	-6	-	18 Jul 1998	44	-
30 May 1998	-5	-	19 Jul 1998	45	0.2
31 May 1998	-4	2.8	20 Jul 1998	46	-
01 Jun 1998	-3	-	21 Jul 1998	47	3.4
02 Jun 1998	-2	39.6	22 Jul 1998	48	0.2
03 Jun 1998	-1	23	23 Jul 1998	49	2.4
04 Jun 1998	0	-	24 Jul 1998	50	-
05 Jun 1998	1	0.4	25 Jul 1998	51	-
06 Jun 1998	2	4	26 Jul 1998	52	3
07 Jun 1998	3	5.8	27 Jul 1998	53	0.6
08 Jun 1998	4	9.8	28 Jul 1998	54	-
09 Jun 1998	5	0.4	29 Jul 1998	55	0.8
10 Jun 1998	6	0.2	30 Jul 1998	56	5.8
11 Jun 1998	7	1.8	31 Jul 1998	57	-
12 Jun 1998	8	-	01 Aug 1998	58	-
13 Jun 1998	9	4.8	02 Aug 1998	59	-
14 Jun 1998	10	1.8	03 Aug 1998	60	0.8
15 Jun 1998	11	11.2	04 Aug 1998	61	0.2
16 Jun 1998	12	-	05 Aug 1998	62	-
17 Jun 1998	13	3	06 Aug 1998	63	-
18 Jun 1998	14	11	07 Aug 1998	64	-
19 Jun 1998	15	0.2	08 Aug 1998	65	-
20 Jun 1998	16	2.6	09 Aug 1998	66	-
21 Jun 1998	17	-	10 Aug 1998	67	-
22 Jun 1998	18	-	11 Aug 1998	68	-
23 Jun 1998	19	2.2	12 Aug 1998	69	0.4
24 Jun 1998	20	0.2	13 Aug 1998	70	-
25 Jun 1998	21	0.6	14 Aug 1998	71	1.6
26 Jun 1998	22	5.4	15 Aug 1998	72	6
27 Jun 1998	23	16.4	16 Aug 1998	73	-
28 Jun 1998	24	-	17 Aug 1998	74	-
29 Jun 1998	25	-	18 Aug 1998	75	-
30 Jun 1998	26	-	19 Aug 1998	76	-
01 Jul 1998	27	-	20 Aug 1998	77	0.4
02 Jul 1998	28	-	21 Aug 1998	78	6
03 Jul 1998	29	-	22 Aug 1998	79	0.4
04 Jul 1998	30	-	23 Aug 1998	80	30.6
05 Jul 1998	31	-	24 Aug 1998	81	2.6
06 Jul 1998	32	0.6	25 Aug 1998	82	2.2
07 Jul 1998	33	-	26 Aug 1998	83	2
08 Jul 1998	34	0.4	27 Aug 1998	84	-
09 Jul 1998	35	-	28 Aug 1998	85	0

## 8.2 Analytical results

### 8.2.1 Herbicide concentrations in surface water

Table 9: Glyphosate in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	3.7	0.5	1.6	1.93
10-Jun-98	15.2	15.3	6.7	12.40
11-Jun-98	3.8	6.1	2.4	4.10
15-Jun-98	1.9	1.8	0.8	1.50
16-Jun-98	1.1	1.4	0.8	1.10
18-Jun-98	3.2	3.5	0.9	2.53
22-Jun-98	1.6	2.3	1.1	1.67
29-Jun-98	1.9	2.3	1.1	1.77
24-Aug-98	0.8	NS	NS	0.80

Table 10: Diuron in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	13	ND	ND	13
10-Jun-98	210	130	60	133
11-Jun-98	110	80	40	77
15-Jun-98	60	40	ND	50
16-Jun-98	50	30	10	30
18-Jun-98	100	40	ND	70
22-Jun-98	10	50	10	23
29-Jun-98	60	40	ND	50
24-Aug-98	ND	NS	NS	ND

Table 11: Atrazine in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	90	70	100	87
10-Jun-98	860	1150	1280	1097
11-Jun-98	630	920	1020	857
15-Jun-98	140	500	470	370
16-Jun-98	340	420	600	453
18-Jun-98	400	490	640	510
22-Jun-98	560	920	850	777
29-Jun-98	320	650	610	527
24-Aug-98	10	NS	NS	10

Table 12: Oxadiazon in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	<20	<20	<20	<20
10-Jun-98	<20	<20	<20	<20
11-Jun-98	<20	<20	<20	<20
15-Jun-98	<20	<20	<20	<20
16-Jun-98	<20	<20	<20	<20
18-Jun-98	<20	<20	<20	<20
22-Jun-98	<20	<20	<20	<20
29-Jun-98	<20	<20	<20	<20
24-Aug-98	<20	NS	NS	<20

Table 13: Oryzalin in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	<10	<10	10	<10
10-Jun-98	<10	10	10	<10
11-Jun-98	10	<10	<10	<10
15-Jun-98	<10	<10	<10	<10
16-Jun-98	<10	<10	<10	<10
18-Jun-98	<10	<10	<10	<10
22-Jun-98	<10	<10	<10	<10
29-Jun-98	<10	<10	<10	<10
24-Aug-98	<10	NS	NS	<10

Table 14: Isoxaben in surface water samples

Date	Upper trench $\mu\text{g.L}^{-1}$	Middle trench $\mu\text{g.L}^{-1}$	Lower trench $\mu\text{g.L}^{-1}$	Mean $\mu\text{g.L}^{-1}$
08-Jun-98	ND	ND	ND	ND
10-Jun-98	<10	<10	<10	<10
11-Jun-98	<10	<10	<10	<10
15-Jun-98	ND	ND	ND	ND
16-Jun-98	ND	ND	<10	<10
18-Jun-98	<10	ND	ND	<10
22-Jun-98	<10	<10	ND	<10
29-Jun-98	ND	<10	<10	<10
24-Aug-98	ND	NS	NS	ND

## 8.2.2 Herbicide concentrations in the lower formation

Table 15: Concentrations in formation material sampled on 03 July 1998, day 29

Herbicide	Middle block $\mu\text{g.kg}^{-1}$	Lower block $\mu\text{g.kg}^{-1}$
Glyphosate	ND	ND
Diuron	200	220
Atrazine	280	340
Oxadiazon	200	310
Oryzalin	<10	20
Isoxaben	NA	NA

Table 16: Concentrations in formation material sampled on 27 August 1998, day 84

Herbicide	Upper block $\mu\text{g.kg}^{-1}$
Glyphosate	ND
Diuron	160
Atrazine	270
Oxadiazon	330
Oryzalin	10
Isoxaben	NA