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Potential Contamination of Surface and Groundwaters Following Herbicide Application to a Railway

by

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Summary

Water quality monitoring of surface and ground waters has demonstrated that there is disproportionate pollution by herbicides applied to hard surfaces. Railways have been identified as potential contributors to this pollution, but there is a lack of data to support this theory.

A small-scale study previously demonstrated that herbicides could leach through railway ballast, but the study was not representative of reality. The aim of this study was to investigate the potential for herbicides to leach to surface and groundwaters following application to a railway under realistic circumstances.

Several herbicides (glyphosate, atrazine, diuron, oxadiazon, oryzalin, imazapyr and isoxaben) were applied to a 750 m length of railway line mimicking normal application procedures. Piezometers were used to sample groundwater at monthly intervals, and surface water was sampled in response to rainfall events.

The results of the study indicate that, under the environmental conditions of the study, glyphosate, atrazine, diuron, oxadiazon, oryzalin, imazapyr and isoxaben are unlikely to leach to ground or surface waters.

It is possible that the dry, warm weather following application may have enhanced herbicide degradation, and the potential for leaching in the winter and spring was hindered by the lower than average rainfall. The distance between the treated area and sample collection points may also have contributed to the apparent lack of herbicide leaching.

Recommendations include an investigation of railway formations for classification into types, and research into the hydrology of railways to improve the ability to predict herbicide leaching following application to railways.

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1 INTRODUCTION

Weed growth on railways can damage the engineered structure and create a health hazard, and their control is necessary to ensure a safe working environment.

The method used for applying herbicides to railways, largely depends on the status of the line. A dedicated spray train was used to control weeds on mainlines until 1999. Subsequently, weed control on mainlines has been by way of a multi-purpose vehicle (MPV) fitted with a Weedspray module. Smaller sidings and short stretches of line are sprayed using a boom (commonly 2 – 4 m wide) that can be housed on a variety of vehicles (e.g. rail trolley, rail adapted truck, standard engine and carriage, tractor). A knapsack is used to spray station areas.

This year, the only herbicides used on railways were glyphosate and diuron, but in the past other compounds have been used including imazapyr, mecoprop and 2 4-D, and atrazine until the early 1990s. Water quality monitoring studies in the 1990s demonstrated that of those pesticides exceeding the water quality standard of 0.1 μgL^{-1}, the most common were herbicides that were exclusively or partly used for non-agricultural purposes. Roads and railways are primary non-agricultural users of herbicides and the potential for contaminated runoff from railways to pollute water sources has been recognised (Cocker, 1996).

Field data to support the theory of water contamination by herbicides applied to railways was lacking. A pilot study by Heather *et al.* (1998) on a section of disused railway indicated that herbicides could be detected in drainage water (up to *ca*. 800 μgL^{-1}) in close proximity to the track. However, this study did not utilise a realistic application method, the study was performed over a small length of track (*ca.* 50 m), and pollution of groundwater was not investigated. To obtain field data, a larger scale study was required that employed realistic herbicide application methods, and that monitored ground and surface waters.

The Soil Survey & Land Research Centre was therefore commissioned by the Environment Agency to investigate the potential for herbicides applied to railways to contaminate surface and groundwaters. The study was performed on a working railway track using normal spray practice, emulating real-life conditions as close as practically possible.

This report describes the study development, the study site, monitoring methodology, results and discussion. Recommendations are also included for research areas that would enhance the ability to predict herbicide leaching following application to a railway.

2 STUDY SITE

To monitor potential herbicide leaching to surface and groundwaters, for practical purposes, it was necessary that the study site have a shallow groundwater. Furthermore, open access to the line and surrounding land was also a necessity.

Initially, the aim of the study was to monitor the fate of herbicides applied to a railway by the spray train. Identification of potential monitoring sites was therefore determined by spray train activity, however permission to gain access to every possible site was not forthcoming.

A suitable study site that was not covered by the spray train, but for which access was readily achievable was therefore identified near Gotham on the line between Nottingham and Loughborough NGR (SK 557 295 to SK 555 291). The line was owned by a private company, Great Central Railways (Nottingham), who run steam and diesel trains on the line, but infrequently. The line was ‘double track’ width, but only one set of tracks remained.

The line dissected arable farmland, growing crops such as oil seed rape, linseed and wheat. The underlying soil was alluvium.

3 METHODOLOGY

3.1 Selection and Application of Herbicides

Seven herbicides (glyphosate, atrazine, diuron, oxadiazon, oryzalin, isoxaben and imazapyr) were applied to a 750 m stretch of the railway line. Six of these herbicides (glyphosate, atrazine, diuron, oxadiazon, oryzalin and isoxaben) have been subject to previous research (Heather *et al.*, 1998, Shepherd and Heather, 1998). Imazapyr, the additional herbicide, has been used to treat weeds on railways in the past.

The section of ‘double track’ where a line had been removed had not been subject to weed control for several years, but due to the imminent (post-study) re-installation of this line, this area needed to be cleared of vegetation. The extent of weed growth in this area was immense and not representative of ‘normal’ conditions. It was therefore necessary to strim and remove excess vegetation before herbicide application.

The herbicides were applied at label-advised rate (Table 1) on 6 September 1999 using a 6 m boom, mounted on to a tractor. The tractor was driven down the middle of the track, with the boom extending over the position of both tracks. This is comparable to the method normally used by the site owners, being a boom attached to a railtruck. Oryzalin, isoxaben and oxadiazon were applied separately. Diuron and glyphosate were tank mixed before application – a common procedure for these herbicides, as were atrazine and imazapyr. Between applications, the holding tank and spray lines were rinsed out with water which was sprayed off within the study site to ensure all herbicide measured out was actually applied.

	Application rate gha^{-1} a.i.
Atrazine	3000
Diuron	2700
Glyphosate	3420*
Oxadiazon	4500
Oryzalin	1728
Isoxaben	75
Imazapyr	750

*Accounts for that glyphosate present in the oxadiazon product

Table 1 Herbicide application rates

3.2 Groundwater Sampling

Permission to install equipment was obtained from the landowner on the condition that it did not interfere with his working the land. This restricted the placement of piezometers to land between the edge of the farm track and the ditch paralleling the railway (Figure 1).

Piezometers consisted of 0.05 m diameter plastic pipe, capped by a coupler and access plug. These were installed by digging up the first 0.5 m of ‘soil’ containing pieces of brick, glass and other material (most probably discarded during the construction of the railway). In the underlying, undisturbed soil, a 0.1 m diameter hole was augered to the required depth. A piezometer tube was placed in the hole into a layer of silica sand. The hole was then back-filled with bentonite, bar the top 0.3 m which was back-filled with ‘undisturbed’ soil taken from the hole.

Two piezometer nests were installed on either side of the embankment, approximately 20 m apart. Piezometer nests on the eastern side of the embankment were installed to depths of approximately 2 m and 1.5 m. Two metres represents the depth to which piezometers could practically be installed and lay within the permanent groundwater. Piezometers installed to 1.5 m lay within the seasonal groundwater table but were below the base of the drainage ditch. The drainage ditch on the eastern flank of the embankment was approximately 1.25 m deep thus groundwater was not sampled above this depth.

The ditch to the west of the embankment was approximately 0.5 m deep thus a shorter piezometer, 0.8 m deep, was installed in addition to 2 m and 1.5 m piezometers. Four piezometers were installed at each depth within a nest to enable sufficient volume of sample to be collected for analysis (Figure 1).

A thin piece of tubing was placed into each piezometer to enable water collection via a suction pump without cross contamination. Distilled water was used to rinse through tubing of the suction pump between sample collections. Water was evacuated from the piezometers the day before sampling to allow the samples to ‘recharge’ with fresh groundwater. Samples from each piezometer were collected separately into glass bottles and stored in a cool box for transport to the laboratory. On return to the laboratory, samples were decanted into amber glass bottles and stored at –20 °C until dispatch to the relevant laboratories for analysis. Any excess water from individual piezometer samples was frozen should it be required for analysis at a future date.

3.3 Surface Water Sampling

The ditches draining the railway embankment were transient and discharged into a transient field drain. The field drain passed through a single field before discharging into a permanent stream. Samples from the field drain and stream were taken manually, up- and downstream from the inlets of interest. An automatic water sampler, triggered by a float switch, was used to collect samples from the railway drainage ditch; flow was monitored using a Starflow doppler and pressure transducer device with internal logger. A plan view of the sampling sites is given in Figure 1. All samples were stored frozen in amber glass bottles.

3.4 Sampling Protocol

Control samples were taken prior to herbicide application on the morning of 6 September 1999 from piezometers (where possible) and the stream. The drainage and field ditches were dry at this time so no control samples were taken from these sites. Samples were also taken the following morning.

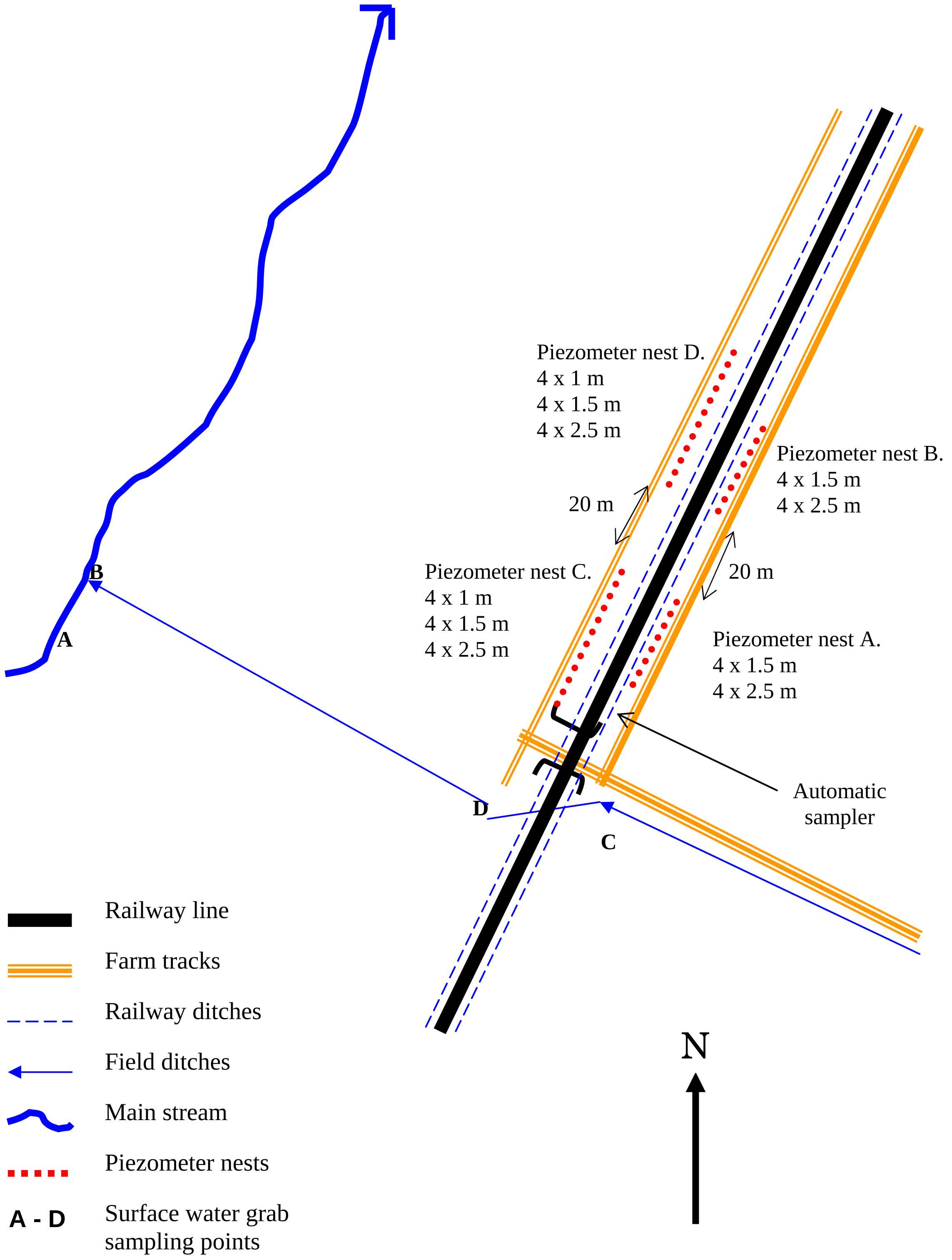

Figure 1 Diagrammatic representation of the study site detailing sampling points. (Not to scale).

Surface water samples were taken when surface water was present. Groundwater samples were taken at approximately monthly intervals from all piezometers where water was present. Samples obtained from within piezometer nests from the same depth were bulked for analysis, with the exception of a single piezometer, C4. It was noted that the recharge time of this piezometer was significantly greater than all other piezometers, thus the hydrological connection most probably differed, and may have been influenced by preferential flow. A detailed hydrological study, beyond the scope of the current study, would have been necessary to confirm this theory. Samples from this piezometer were not bulked with other piezometer water but were treated separately.

Samples were sent to analytical laboratories in March /April 2000.

3.5 Chemical analysis

Samples were sent in cool boxes to the relevant laboratories; namely the Environment Agency for glyphosate, imazapyr, atrazine and diuron, Aventis Environmental Science for oxadiazon, and Dow AgroSciences for isoxaben and oryzalin. For some samples, Aventis also analysed for atrazine and diuron.

The detection limits varied between compounds, and, for some samples, 2 laboratories analysed for the same compounds. The detection limit was dependent on the volume of water available for analysis, but, with some occasional exceptions, detection limits for all compounds were 0.1 µgL^{-1} or less. Detection limits for the compounds are tabulated below.

Compound	Detection limit (µgL^{-1})
Glyphosate	< 0.1^{+}
Imazapyr	< 0.02
Diuron	< 0.02
Atrazine	< 0.07*
Oxadiazon	< 0.1
Oryzalin	
Isoxaben	

$^{+}$ 1 sample < 0.2 µgL^{-1}.

*Mean value. Range <0.03 to < 0.27 µgL^{-1}; 90 % < 0.1 µgL^{-1}.

Table 2 Detection limits for the chemical analysis of the applied herbicides.

3.6 Air Temperature and Rainfall

Air temperature was measured every 2 hours and recorded via a Delta-T 3000 logger. A tipping bucket rain gauge was also connected to the logger to record rainfall every 0.2 mm. There were two occasions when the rain gauge did not function, and daily rainfall readings measured at SSLRC's Shardlow laboratory (6 miles from the site) were used to cover these short periods.

4 RESULTS

4.1 Air Temperature and Rainfall

On the day of spraying (6th September 1999), the daily mean air temperature was 18 °C, with a maximum of 26 °C. In the following week, maximum temperatures were in the order of 20 °C, with a mean of 16 °C. Light drizzle fell on the day following application (0.8 mm), and in the week following application rainfall totalled 3.2 mm. The first rainfall event exceeding 10 mm occurred 2 weeks after application (10.2 mm on 20th September).

Mean daily air temperature and total daily rainfall are illustrated in Figure 2. The temperature range and total rainfall for each month are given in Table 3.

	Total rainfall (mm)	Air temperature (°C)		
		Mean	Maximum	Minimum
September	58	14.6	25.9	4.9
October	55.6	10.4	20.4	-0.8
November	28.6	7.8	14.8	-0.9
December	47.4	4.3	6.9	1.8
January	28.8	5.0	8.2	1.6
February	61.9	6.1	9.5	2.5
March	20.6	7.2	11.7	2.4
April	96	7.7	12.2	3.1
May	71.8	11.7	16.8	7.2
June	36.4	15.2	19.9	10.1
July	47.4	15.1	20.4	10.1

Table 3 Monthly rainfall and air temperature

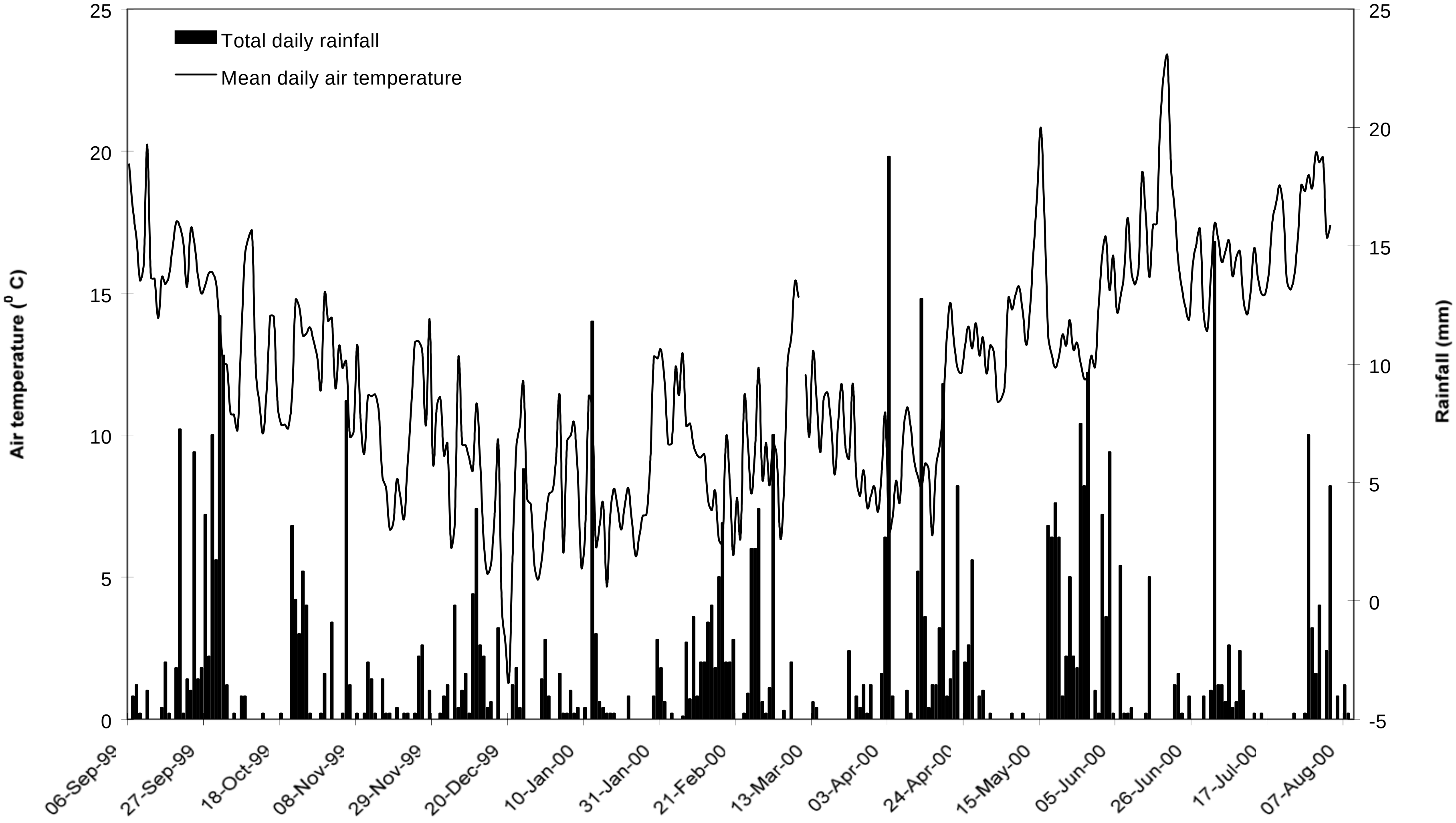

Figure 2 Total daily rainfall and mean daily air temperature during the study period.

4.2 Hydrology

Groundwater levels are given as a height above an arbitrary datum (the base of the drainage ditch minus 100 m). The measured groundwater levels at each piezometer nest were combined to give a mean. The mean groundwater level is shown in relation to rainfall in Figure 3. During the study period, groundwater was lowest at 98.85 m above the datum during September when the herbicides were applied, and slowly wetted up to a maximum of 99.87 m in April giving a range of approximately 1 m. In the first 6 months, the groundwater rose by 0.48 m after 280.3 mm of rain had fallen. This compares to a groundwater rise of 0.54 m in only 2 months (March and April) after only 116.6 mm of rain had fallen. The groundwater then receded in the following 5 months by 0.57 m, in which time a further 251.6 mm of rain fell.

During the experimental period, there were only 3 occasions when surface water was present in the drainage ditches;

- 3rd March 2000 following 10 mm rainfall on 2nd March,
- 3rd and 4th April 2000 following 19.8 mm of rainfall on 3rd April (and 6.4 mm on 2nd April), and
- 13th and 14th April (rainfall for 12th – 14th April was 14.8, 3.6 and 0.4 mm respectively).

4.3 Herbicide Detection

Due to the differences in detection limits, discussion is largely limited to whether or not compounds are detected at, or above, the drinking water standard (0.1 µgL^{-1}).

4.3.1 Control Samples

Analysis of groundwater sampled the day prior to spraying indicated that none of the compounds used were present at concentrations above 0.1 µgL^{-1} (glyphosate (<0.1), atrazine (<0.09), diuron (<0.02), oxadiazon (<0.1), oryzalin, imazapyr (<0.02), isoxaben all in µgL^{-1}).

Atrazine, diuron, oxadiazon, oryzalin, imazapyr and isoxaben were not detected in the control surface water samples. However, in surface waters glyphosate was detected at concentrations of 0.15 and 0.12 µgL^{-1} in the control samples.

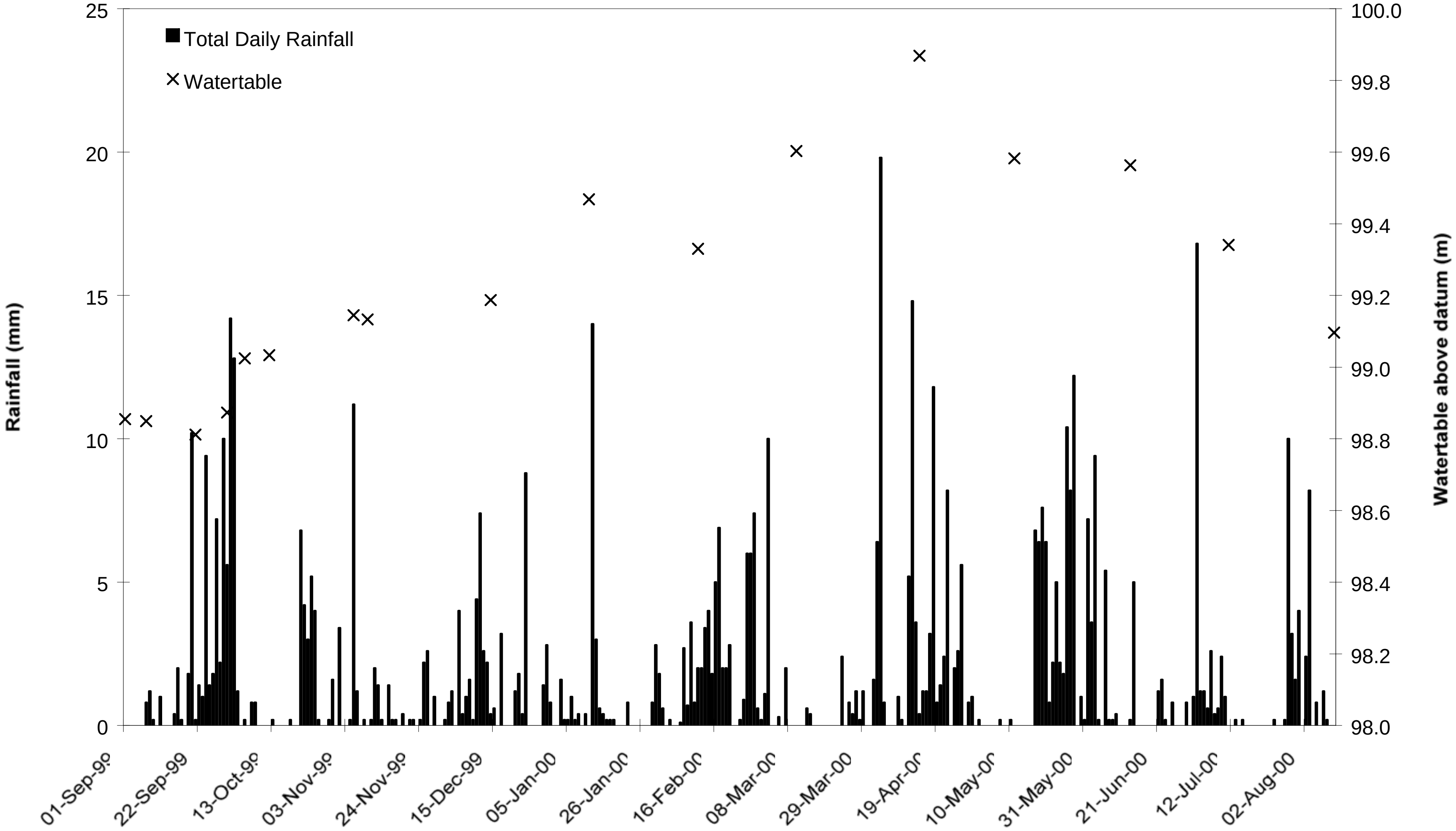

Figure 3 Watertable height above the drainage ditch in relation to rainfall

4.3.2 Piezometers

Diuron and glyphosate were below their limits of detection (0.02 and 0.1 μgL^{-1} respectively) in all groundwater samples. Imazapyr was below the limit of detection (0.02 μgL^{-1}) for all samples bar one where there was a positive detection of 0.08 μgL^{-1}. There were no positive detections of atrazine, however, there were 6 occasions when the detection limit exceed 0.1 μgL^{-1} (range = < 0.11 to < 0.27 μgL^{-1}) due to the small sample volume. On these occasions, samples taken from other piezometers had been analysed to detection limits below 0.1 μgL^{-1} hence it is possible to assess the likelihood of samples analysed to levels greater than the drinking water standard actually exceeding 0.1 μgL^{-1}.

There was one positive detection of oxadiazon in a single piezometer at 0.1 $\mu g\ L^{-1}$. The same sample was analysed by Avenits for atrazine, and a concentration of 5.2 $\mu g\ L^{-1}$ was detected. This compares to a concentration of < 0.11 $\mu g\ L^{-1}$ for the same sample analysed by the Environment Agency. Spare sample kept in frozen storage at Shardlow was sent to EA for re-analysis. The result returned was an atrazine concentration of < 0.03 $\mu g\ L^{-1}$. (The difference in detection limit was due to the difference in sample volumes).

4.3.3 Surface Water

Following herbicide application to the railway, imazapyr, glyphosate and atrazine were below their limits of detection (0.02 μgL^{-1}, 0.1 μgL^{-1} and mostly < 0.1 μgL^{-1} respectively) in drainage ditches adjacent to the railway and in the main stream. On one occasion the detection limit for glyphosate was 0.2 μgL^{-1}, but this was a duplicate of another sample where glyphosate was not detected and the detection limit was 0.1 μgL^{-1}.

There were several occasions when diuron was positively detected in the stream with approximately half the samples containing concentrations at or above 0.1 μgL^{-1}. The maximum detection of diuron was 0.68 μgL^{-1}. There were no positive detections of diuron in samples taken from the drainage ditches adjacent to the railway. There were no results for oxadiazon in surface waters as the samples were sent for analysis prior to the presence of surface water in the drainage ditches.

	Main stream			Drainage ditch			Groundwater		
	Control	Day 1	Other	Control	Day 1	Other	Control	Day 1	Other
Atrazine	<0.1	<0.1	<0.1	n/a	n/a	<0.1	<0.1	<0.1	<0.1
Diuron	<0.02	<0.02	0.03 - 0.68	n/a	n/a	<0.02	<0.02	<0.02	<0.02
Glyphosate	0.13*	<0.1	<0.1	n/a	n/a	<0.1	<0.1	<0.1	<0.1

Oxadiazon	<0.1	<0.1	n/a	n/a	n/a	n/a	<0.1	<0.1	0.1
Oryzalin				n/a	n/a				
Isoxaben				n/a	n/a				
Imazapyr	<0.02	<0.02	<0.02	n/a	n/a	<0.02	<0.02	<0.02	0.08

* Mean of 2 samples. n/a Water was not available for analysis

Table 4 Summary of herbicide analysis in the main stream, railway drainage ditch and groundwater.

5 DISCUSSION

The results have demonstrated that, under the climatic conditions of the study period, the application of glyphosate, atrazine, diuron, oxadiazon, oryzalin, imazapyr and isoxaben to a railway embankment at label application rate is unlikely to result in these pesticides contaminating ground or surface waters. Although there were positive detections of both glyphosate and diuron in the main stream, it is unlikely that the railway site was the source of contamination.

Glyphosate was detected above 0.1 µgL^{-1} (mean = 0.13 µgL^{-1}) in the main stream on the day prior to spraying, thus this contamination could clearly not have resulted from application to the railway. There were several potential sources of glyphosate to the surface water ditches; namely, adjacent agricultural fields, an industrial works upstream, and the ditch itself where glyphosate was occasionally used for aquatic weed control. Whatever the source, it was short-lived as there was no positive detection of glyphosate in the samples taken the morning following application at the railway site.

Diuron was detected in the main stream up- and downstream (A & B respectively in Figure 1) from the drainage ditch inlet (means of 0.22 and 0.15 µgL^{-1} respectively) only 2 weeks after the railway had been sprayed. At this time, the groundwater was low (Section 4.2), there had been less than 20 mm of rainfall since herbicide application, and there was no surface water connection between the drainage ditch adjacent to the railway and the main stream. It is therefore unlikely that the railway was the source of diuron detected in these samples. Nevertheless, it is possible that the diuron detected in the stream could have emanated from a hard surface (for example, road or industrial works) upstream from the study site, because on the day prior to sampling, 10.2 mm of rain fell which has previously been shown to be sufficient to remove herbicide from concrete and asphalt surfaces (Heather *et al.*, 1999) and diuron is commonly used in these non-agricultural areas.

Samples taken from the stream on 3rd March 2000, contained mean diuron concentrations of 0.49 & 0.04, and 0.68 & 0.52 µgL^{-1} up- and downstream respectively from the field drain inlet, but there was no significant difference between the means ($p < 0.05$). The difference in concentration up and down stream of the inlet would most probably be natural variation in sampling/analysis. Diuron concentrations in the drainage ditch adjacent to the railway were less than 0.02 μgL^{-1}, thus, considering all the evidence, it is unlikely that the railway was a source of diuron in this instance. Again, it is possible that the diuron was the result of loss following application to a hard surface, as there had been heavy rainfall (*ca.* 10 mm) prior to sampling, but the source was more likely to have been areas feeding directly into the stream than the railway under investigation. The lower concentrations of diuron (*ca.* 0.07 μgL^{-1}) detected a week later, and lower still in April (< 0.1 μgL^{-1}) suggest that the diuron source is limited. This pattern of decreasing loss with successive rain events compliments that pattern observed in previous investigations of herbicides applied to a roadside (Heather *et al.*, 1999). The absence of diuron in the railway ditch (< 0.02 μgL^{-1}) at the times of detection in the main stream, suggests that diuron application to the railway embankment was unlikely to contribute to its presence in the main stream.

In groundwater, only imazapyr and oxadiazon were detected ‘positively’ (0.08 $\mu g\ L^{-1}$ and 0.1 $\mu g\ L^{-1}$ respectively). Both detections were in a single piezometer and on different dates (February 2000 and November 1999 respectively). On the dates of these detections, groundwater samples taken from all other piezometers indicated imazapyr concentrations were below 0.02 μgL^{-1} and oxadiazon concentrations were below 0.1 $\mu g\ L^{-1}$.

Imazapyr has a low K_{oc} (*ca.* 1 mlg^{-1}), a medium DT_{50} (90 days) and a high solubility (*ca.* 1000 mgL^{-1}), thus the compound would ordinarily result in being classed as highly mobile in soils. However, previous studies have demonstrated that these physico-chemical properties cannot always be used as an indicator of herbicide mobility on hard surfaces (Heather *et al.*, 1998; Shepherd & Heather, 1999), and other factors such as application rate and the characteristics of the surface treated may be influential in determining the rate of loss. The application rate of imazapyr is only 750 gha^{-1}. The K_{oc} of atrazine (*ca.* 100 mlg^{-1}) is not as low as for imazapyr, but the application rate is much higher (3000 gha^{-1}). It could be expected that, if herbicides had been leached, atrazine would also be detected, but concentrations were < 0.07 μgL^{-1} in the sample in question but more research is required to assess the impact of application rate versus K_{oc} and solubility with regard to herbicide losses from hard surfaces. Given that imazapyr was not detected in the other piezometers, and there was no positive detection of atrazine, the ‘detection’ of imazapyr at 0.08 μgL^{-1} should be treated with caution. Nevertheless, if the imazapyr concentration was 0.08 $\mu g\ L^{-1}$ this would still be within the permitted drinking water standards.

Oxadiazon has a much higher K_{oc} than atrazine (3200 *cf.* 100) thus it could be expected that atrazine would leach preferentially to oxadiazon. In the same sample, Aventis detected 5.2 µg L^{-1} atrazine but the Environment Agency detected only < 0.11 µg L^{-1} of atrazine in this sample. Spare sample was sent for re-analysis to the EA who reported atrazine concentrations of < 0.03 µg L^{-1}. It is possible that some degradation of atrazine may have occurred during the year it was in storage but overall, the results suggest that atrazine concentrations were less than 0.1 µg L^{-1}. There were no other positive detections of oxadiazon during the course of the study suggesting that the analysis of the sample reporting oxadiazon concentrations of 0.1 µg L^{-1} is questionable. Furthermore, as this value is equal to the limit of detection it cannot be treated with confidence.

The overall non-detection of herbicides in groundwater suggests that, under the environmental conditions of the study, herbicide leaching was minimal. In the absence of throughflow, pesticides will not leach to pollute ground or surface waters, thus the quantity of rainfall, and its timing since application may be important factors in determining whether or not, or by how much, a pesticide will leach after application. The fate of applied herbicides may also depend on air temperature, in relation to microbial activity and associated degradation.

In examining these factors affecting herbicide leaching, it is necessary to assess whether or not rainfall during the study period was ‘typical’. This was achieved by comparing measured rainfall at Gotham to the 29 year average for Sutton Bonnington, the closest Meteorological Office Station to the study site (< 3 miles).

In the 2 months prior to herbicide application, rainfall was approximately 70 % of the 29 year average (80 mm *c.f.* 112 mm). Combined with warm temperatures (mean minimum = 11 °C and mean maximum = 20 °C for the 29 year average), this low rainfall would result in the drying out of the soil, as reflected by the low groundwater table at the time of application (Figure 3). The light rain that did fall within the 3 weeks (4 mm), in association with warm temperatures (mean = 15 °C) would be more likely to encourage microbial activity, and hence degradation, than to enhance leaching of the herbicides.

	Monthly rainfall (mm)		% of long term average
	29 yr mean	Gotham ‘99-‘00	
August	58.7	56.6	96.4

September	48.5	58.0	119.6
October	45.5	55.6	122.2
November	49.7	28.6	57.5
December	51.1	47.4	92.8
January	53.4	28.8	53.9
February	46.2	61.9	134.0
March	46.7	20.6	44.1
April	44.8	96.0	214.3
May	55.4	71.8	129.6
June	53.7	36.4	67.8
July	53.2	47.4	89.1

Table 5 A comparison of rainfall at the study site to the 29 year long term average at Sutton Bonnington

Although September and October were wetter than the long term average (Table 5), November and January were 58 and 54 % drier respectively. Likewise, February was 34 % wetter than the 29 year mean, but March received less than half (44 %) of the long-term average. Overall, from application time to March, rainfall was only 88 % of the long-term average. There was a single rain event in March (3rd March 2000) that produced some surface water in the ditch, but in April, when rainfall was more than double the long-term average, surface water was present on 2 occasions.

The less than average rainfall may not have been sufficient to leach the herbicides through the embankment to groundwater, and degradation may have continued to occur even if there was some downward movement. Degradation may have been encouraged by the favourable temperature and moisture conditions for microbial activity.

The absence of any positive detections of herbicide in groundwater or surface water adjacent to the railway may also have been influenced by the constituent materials, and/or the topography of the land it was applied to, i.e. a 2.5 m high embankment.

Inspection of the railway formation indicated that there was a clay cap approximately 75 cm below the ballast, as was found at the site of the pilot railway study. The hydrology of railways is not known thus, based on general knowledge of hydrology and the results of previous studies, assumptions were made regarding the hydrology of the railway at Gotham; namely that water would infiltrate vertically to the clay cap where it would then flow laterally through the side of the embankment. The washoff studies demonstrated a delay in throughflow after rainfall initiation (REF) indicating that ballast had some storage capacity for water, thus it could be expected that for rain events of up to approximately 3 mm very little, if any, throughflow would occur. For significant rain events of 10 mm or greater it could be expected that there would be sufficient water to produce lateral flow over the clay cap. The absence of lateral flow and surface water for the majority of the larger rain events suggests that the clay cap may no longer be an efficient hydrological barrier. If cracks were present in the clay, substantial vertical infiltration would need to occur before water reached the water table. This travel time would greatly delay, or could even negate, herbicide leaching to groundwater.

The efficiency of the clay cap may depend on the ambient ‘soil’ moisture. For example, in the pilot railway study, the formation in which the trenches were located was sufficiently compact to retain water for a few days. Rainfall preceding and following the time of application was particularly heavy (REF) thus the clay may have been fully expanded, minimising, or eliminating, cracking. Conversely, in a dry summer (as occurred during the current study), clay could contract introducing cracking. Cracking clay is an important hydrological feature in pesticide leaching in an agricultural environment (REF) but on a railway, cracking in the clay cap would merely allow water through to the subsoil, and the consequences of preferential flow may not be apparent, unless the underlying subsoil was clay and also cracked.

The majority of railways in the UK were built in Victorian times, thus it is probable that where a clay cap exists, it is less efficient than when first built. However, the extent of the use of a clay cap in a rail line infrastructure is unknown thus extrapolation of this theory cannot be made with confidence. Knowledge of the infrastructure of railways across the UK would greatly assist in predicting the potential for applied herbicides to pollute ground and surface waters.

During the pilot study, over the 2 days prior to spraying, 62.6 mm of rain fell and local water tables were high as indicated by the presence of water in the trench dug the day before herbicide application. Although no rain fell on the day of application, within 3 days 20 mm of rain had fallen, with a total of 81.8 mm of rain falling in less than 4 weeks since herbicide application. The controlled washoff studies also demonstrated a greater loss of herbicide with increasing rainfall applied. The absence of herbicides in leachate where water has drained through a relatively large section of ballast that has received lower than average rainfall contrasts to the pilot study where there was minimal potential for downward leaching combined with heavy rainfall, and herbicides were detected in drainage waters. Atrazine is a very mobile compound that does not degrade rapidly, thus it could be expected that if there was water movement to ground or surface waters that this compound would be detected; a process that has been demonstrated in previous studies (Hollis *et al.*; Shepherd & Heather, 1999). The absence of the detection of atrazine in particular suggests that water movement through the railway embankment was minimal during the experimental period.

The experimental design of both the pilot study and controlled washoff studies was such that there was a short distance / depth of ballast between the source of the herbicide and the collection of throughflow / runoff. In the controlled washoff study, the minimum distance between area sprayed and throughflow collection was 0 m, with a minimum depth of 0.4 m. In the pilot study, the minimum depth was 0 m, with a minimum distance of approximately 1.5 m between herbicide source and throughflow / runoff collection. This contrasts to the current study where the minimum depth between herbicide source and runoff collection was approximately 2.5 m, and the minimum distance approximately 3 m.

The results of the pilot railway study, the controlled washoff study and the current study suggest that rainfall volume and / or the distance between herbicide source and sample collection could influence the loss of herbicides from ballast. Whether or not there is a maximum depth of ballast at which herbicides will not be detected in leachate may depend on a variety of factors, such as constituent material, rainfall quantity and intensity, and the physico-chemical characteristics of the compound. More detailed investigation would be required to understand the full relevance of these factors.

6 CONCLUSIONS

- The detection limit of the herbicides differed, but, with minor exceptions, they were below 0.1 μgL^{-1} and this did not hinder the interpretation of the results.
- With the exception of a single sample (0.08 μgL^{-1} imazapyr), there were no positive detections of any herbicide applied to the railway in groundwater. When considering all the evidence, it is possible that this ‘positive’ detection is a spurious result.
- There were only 3 occasions when surface water was present in the drainage ditch paralleling the railway. All herbicides were below the detection limit in the drainage ditch.
- Atrazine, oxadiazon, oryzalin, imazapyr and isoxaben were below the limits of detection in the main stream.
- Glyphosate was detected at concentrations > 0.1 μgL^{-1} in the main stream, but as this was present the day before spraying the study site, the railway could not have been the source.
- Diuron was also detected on several occasions in the main stream. However, it was present when there was no surface water connection to the railway site, and/or when diuron concentrations in the drainage ditch were < 0.02 μgL^{-1}. The evidence available strongly suggests that the railway study site was not the source of diuron in the main stream.
- The dry, warm weather following herbicide application may have been conducive to microbial degradation of the compounds.
- The lower than average rainfall and the depth of railway formation may have negated herbicide leaching.
- The results of the current study contrast to those of the pilot railway study. It was noted that the climatic conditions and the distance from herbicide source to collection point were also contrasting and may have influenced the fate of the herbicides following application.
- The prediction of herbicide leaching through railway formations is hindered by a lack of knowledge on the constituent material of the engineered formation and the hydrology of railway environments.

7 RECOMMENDATIONS

A desk study could be undertaken using existing water quality monitoring data (assuming it were available) and the location of rail networks and other hard surface areas, to establish the strength of any correlation between hard surface areas and water pollution by herbicides in the vicinity. If polluting areas are identified, a more detailed, field investigation of these areas could be made to establish the factors that are likely to influence water pollution.

To assess the impact of normal spraying practices on ground and surface waters in the vicinity of railways, it would be advantageous to continue sampling for a period that could encompass a variety of climatic conditions. Furthermore, flexibility within the sampling programme would enable samples to be taken to suit the climatic conditions. For example, it may be beneficial to increase the number of samples taken during wet weather.

In agricultural situations, the soil type is fundamental to predicting herbicide leaching. Knowledge of the composition of railway formations is required to progress with the prediction of herbicide movement through railways. Herbicide leaching is dependent on the local hydrology and the chemical constituents of the ‘soil’; neither of which are known for railway formations. This information could be combined with and/or compared to the local geology to identify areas that may be particularly vulnerable to ground or surface water contamination.

To assess the extent to which the depth of ballast and/or slope is influential in herbicide leaching, lysimeter experiments could be performed. If ground studies demonstrated that the composition of the formation did differ, this could be accounted for the experimental design so the influence of the formation type on herbicide leaching could be assessed. Experiments could also be performed to quantify the sorption capacity of different formation types, providing data that are commonly available for soils. These small-scale experiments would enable a more detailed assessment of the processes of herbicide leaching in a railway formation, which subsequently would enable more accurate predictions to be made.

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