

Appendices

to

**Updated Technical Guidance on HardSPEC Model
Principles and Application for version 1.4.3.2**

Appendix 1.

Summary of the main field and laboratory studies used to support development of the HardSPEC model

A1.1 Compounds used in the studies

The various studies carried out to investigate and quantify losses of herbicides from different man-made hard surfaces and catchments used a range of compounds selected either for their relevance to the hard surface environment or to ensure that a wide range of physico-chemical and application characteristics were taken into account. For all studies except the Sorption Study (Ramwell, 2002), six herbicides were used: atrazine, diuron, oryzalin, oxadiazon, isoxaben and glyphosate. For the Sorption Study, four more compounds: isoproturon, dichlorophen, phenanthrene and fluoranthene were added to the six in order to extend the range of sorption potential investigated. The important characteristics of these compounds are summarised in table A1.1-1.

Table A1.1-1. Characteristics of the compounds used in the various Hard Surface studies.

Compound	Application rate of active ingredient (g ha ⁻¹)	Specific gravity	Solubility (mg l ⁻¹)	Kow	Soil Koc (ml g ⁻¹)	Soil DT50 (days)
Atrazine	3000	1.23	33	219	118	42
Diuron	2700	1.48	36.4	708	218	100
Oryzalin	1730	1.2	2.4	5370	625	63
Oxadiazon	4500	?	10	63096	3200	60
Isoxaben	75	0.58	1.5	7943	767	105
Glyphosate	1800	1.704	116000	0.00002	28000	47
Isoproturon ¹			55	302	147	
Dichlorophen ¹			30	199526	4100	
Phenanthrene ¹			0.6	28840	11979	
Fluoranthene ¹			0.26	144544	41550	

¹ Compound used only for the Sorption Study (Ramwell, 2002)

A1.2 Losses of six herbicides from a kerb and gully-pot drain (Heather *et al*, 1998).

The objectives of this study were to measure direct losses of herbicides from a 'real world' situation and to assess what processes influence the fate of the herbicides after application and during wash-off. Six herbicides (atrazine, diuron, oxadiazon, glyphosate, oryzalin, isoxaben), selected to represent a range of physico-chemical properties and application rates, were applied to the kerb edge of a section of asphalt road. A weir fitted with automatic sampling equipment was used to sample runoff from the outlet of a gully pot drain until 25 mm rain had fallen. The road catchment for the gully pot drain was approximately 112 m². In order to avoid possible saturation of adsorption sites, the six compounds were applied in two groups on separate occasions. Atrazine was included in both application groups so that the effect of the different application dates could be seen. Although rain fell within a few hours of application on both of the application days, the amount was only sufficient to trigger drain flow sampling following the first application. Following this treatment, 3, 5 and 2 mm of rain fell on the day of treatment and the two subsequent days. Mean temperature for the 28 day sampling period was 7.8 °C. Following the second application, only 0.8 mm of rain fell on the day of treatment and there was no further rainfall until the 8th day after treatment when 0.6 mm of rain fell followed by 3.2 mm on each of the two subsequent days (9th & 10th days after treatment). Mean temperature for the 28 day sampling period was 5.8 °C. Conclusions were as follows:

- i. As little as 0.8 mm of rain could initiate herbicide wash-off from hard surfaces, whereas only 2 - 3 mm of rainfall was required to move significant amounts of herbicides out through roadside drains;
- ii. The first 5 - 7 mm of rainfall after application were the most important and caused the most wash-off. For all detected compounds, accumulated wash-off was virtually complete after 13 mm of rainfall;
- iii. Small amounts of glyphosate continued to be washed off the road surface until the end of the study. It is possible that this was also the case for all other applied compounds although the level of analytical quantification was too high to confirm it;
- iv. The extent of wash-off appears to be dependent on the time delay from application to rainfall causing drain flow whereas relative losses of different compounds appear to be functions mainly of K_{OC} and water solubility;
- v. With the exception of avoiding over-spray of drains, the environmental conditions of this study are likely to represent herbicide wash-off under worst-case conditions: strip application to a drained channel in a small catchment with no external dilution. Rainfall shortly after

application could also be considered a realistic worst-case, causing drain flow within six hours of herbicide application.

A1.3 Losses of six herbicides from a disused railway formation (Heather *et al*, 1999).

The objectives of this study were to monitor the concentrations of herbicides leaching from a real railway track bed to the base of the 'soil' formation directly beneath it and to the surface drains directly adjacent to the track. Six herbicides (atrazine, diuron, oxadiazon, glyphosate, oryzalin, isoxaben) 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. The main conclusions of the study were as follows:

- i. 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.
- ii. 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.
- iii. 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.

- iv. There is a significant time lag before quantifiable amounts of herbicide are washed through the railway formation into the adjacent drainage ditches.
- v. 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.
- vi. 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.

A1.4 Factors affecting the loss of six herbicides from hard surfaces (Shepherd & Heather, 1999).

The objectives of this study were to investigate the factors affecting herbicide wash-off from different types of hard surfaces under controlled conditions of rainfall. The removal of six herbicides (glyphosate, isoxaben, oryzalin, oxadiazon, diuron and atrazine) from three different surface types (asphalt, concrete and ballast) was investigated. The selected pesticides were applied individually to each surface type using a modified spray gun. Each surface type had a surface area of 0.54 m² and the ballast surfaces were 0.4 m deep, giving a volume of 0.216 m³ from which drainage was collected. Three replicates of each surface were used. Applications were made in accordance with amenity labels and, where possible, represented typical use. Following application, the surfaces were exposed randomly (within groups) to a natural climate for 6, 12, 24 or 168 hr. Mean half daily temperature during the 168 hour lag time study ranged from 4.5 to 13.2 °C with an average of 8.8 °C. Simulated rainfall (of 5, 10 or 15 mm) was then applied. Samples of run-off were taken at three designated points (First, Middle and End). The study showed that:

- i. Initiation of run-off following the start of rain differed between the different surfaces. Initial run-off from concrete surfaces occurred approximately 50% earlier than from asphalt. Ballast surfaces retained water for a significantly longer period than either asphalt or concrete, mainly because run-off from concrete and asphalt was measured from the surface of the materials whereas from ballast it was measured from the base of a 40 cm deep column.
- ii. Surface type significantly affects the levels of herbicide run-off. On average, across the range of rainfall volumes and rates tested (5 to 15 mm hr⁻¹) and the lag times between application and rainfall (6 to 168 hours), total loss for concrete was 28%, compared to 16

and 13% for asphalt and ballast respectively. Variation in measured losses from replicated concrete surfaces is much greater than that from either asphalt or ballast.

- iii. For all compounds, the highest proportion of total loss occurred during the first 0.66 mm of accumulated rainfall. However, the rate of herbicide loss declined after 2 mm of accumulated rainfall.
- iv. Rainfall volume was a significant factor affecting herbicide losses from all three surfaces. Events with higher volumes of water gave significantly higher losses than events of lower volume. Rainfall rate appeared to be a far less significant factor. Results were variable and only atrazine on asphalt showed significantly increased losses with rainfall rate and then only for the highest rate of 15 mm hr⁻¹.
- v. The interval between herbicide application and initiation of rainfall appeared to have no significant affect on the levels of herbicide loss, except for glyphosate on asphalt. For this situation, glyphosate losses were significantly greater for a short time lag of 6 hours than for other time lags of 12, 24 and 168 hours.
- vi. Under the experimental conditions, only glyphosate on both concrete and asphalt reached a steady state of loss and this occurred after about 6 mm of accumulated rain.
- vii. The limited set of compounds used meant that any statistical analysis is of limited value. However such analysis suggested that both compound water solubility and K_{OC} influence losses but the relationships are weak and vary between surfaces. No significant relationship existed between soil DT₅₀ and loss.
- viii. For concrete and asphalt surfaces, analysis of the masses lost per 250 ml of runoff suggested that:
Glyphosate solubility is so high that all the applied mass would be lost in the first 0.5 mm of rain. The results for both concrete and asphalt show that this is not the case, *which implies that not all the potentially soluble material goes into solution.*
On concrete, compounds with low solubility lose between 1.5 times (diuron) and 19.2 times (oryzalin) more mass in the initial 250 ml of runoff than would be expected from solubility alone. *This implies that some of each compound is washed-off in its non-soluble state.*
On asphalt, all compounds show significantly less initial losses than would be expected if all potentially soluble material was lost. *This implies that there is some adsorption / retention of compounds on the asphalt surface.*
For concrete and to a lesser extent for asphalt, significantly decreasing losses of compound occur for successive 0.5 mm increments of rain. *This implies that EITHER sorption to the surface increases over time OR less 'non-soluble' material is lost over time, OR both.*

A1.5 Herbicide losses from a small urban catchment (Ramwell *et al*, 2000).

The objectives of this study were to monitor herbicide concentrations in drainage outflow from a small, car park sub-catchment of 893 m² within a larger 'urban' catchment of approximately 213 ha and to monitor corresponding concentrations in the receiving stream water 85 m downstream from the drain outfall, after dilution had occurred. The methodology used was similar to the roadside study so the results could be compared. Six herbicides (glyphosate, isoxaben, oryzalin, oxadiazon, diuron and atrazine) were applied to the car park sub-catchment on two occasions 12 days apart and with approximately 60 mm of accumulated rainfall between the applications. Maximum air temperature On the day of spraying mean air temperature was 15 °C and reached a maximum of 23 °C. During the subsequent 12 days between applications, the average temperature was 14 °C. Results from the study showed that:

- i. As with the roadside study (see section 2.2 above), concentrations of atrazine and diuron washed out of the car-park sub-catchment were greater than those of glyphosate, oxadiazon, oryzalin and isoxaben.
- ii. After 15 mm of rainfall, concentrations of both atrazine in drainflow from the car park were greater than those measured in drainflow from the roadside study (160 µg l⁻¹ as opposed to approx. 50 µg l⁻¹). *This was attributed to a higher percentage of the catchment being sprayed in the car park study, and possible longer travel times, hence greater temporary retention in the car park catchment, rendering more available for loss after 15 mm of rainfall.*

In contrast, concentrations of glyphosate in drain flow after 15 mm of rainfall were similar in both the car park and the roadside study (19 µg l⁻¹ as opposed to 16 µg l⁻¹), despite the difference in total herbicide applied. *This may be because, for glyphosate, steady-state losses appear to be achieved after only about 6 mm of accumulated rainfall (see section 2.4) and that losses after 15mm of accumulated rainfall are principally determined by desorption / re-activation of compound held on the hard surfaces present in the catchment.* Comparisons for other compounds could not be made.

- iii. The limited data available suggest that dilution and/or dissipation in the receiving ditch is significant and reduces direct runoff concentrations by at least 7 times. For example, for one specific rainfall event, atrazine concentrations decreased from an average of 75 µg l⁻¹ in drainage from the car park to <10 µg l⁻¹ at the ditch monitoring point. Nevertheless, significant concentrations of applied compounds were measured at the ditch outflow. For atrazine, oryzalin and glyphosate, the maximum concentrations measured were 13, 5 and 9.4 µg l⁻¹ respectively. For isoxaben, diuron and oxadiazon concentrations were always below the lower validation levels of 2, 10 and 20 µg l⁻¹ respectively.

- iv. Significant amounts of all compounds continued to be washed out of the car park sub-catchment even after 58 mm of accumulated rainfall. Concentrations in drainflow from the car park for a rainfall event occurring after 58 mm of accumulated rainfall gave concentrations of 69, 26, <20, 5, 4.9 and <2 μgL^{-1} for atrazine, diuron, oxadiazon, oryzalin, glyphosate and isoxaben respectively. Measured downstream concentrations for the same event were 2.5 and 0.1 μgL^{-1} for oryzalin and glyphosate respectively whereas levels of atrazine, diuron, oxadiazon and isoxaben were all below the lower validation levels of 10, 10, 20 and 2 μgL^{-1} respectively.

A1.6 Potential contamination of surface- and ground-waters following herbicide application to a railway (Ramwell *et al* 2001)

The objectives of this study were to investigate the potential for herbicides applied to an operating railway under realistic circumstances to contaminate local surface and groundwaters. 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. Surface water in ditches adjacent to the railway line and in a local stream into which those ditches drained was sampled in response to rainfall events. On the day of spraying, 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. Conclusions from the study were as follows:

- i. Comparison of results with those from the pilot railway study (see section 2.3 above) is very difficult because of significant differences in the rainfall and temperature patterns between the two studies and the distance from herbicide source to monitoring points. In this study, there was a total of 3.2 mm of rain during the week following application and the first rainfall event exceeding 10 mm occurred 14 days after application. In contrast, during the pilot railway study, a total of 22.4 mm of rain fell during the week after application and rainfall events of 10 mm or more occurred 4 and 15 days after application.
- ii. In the drainage ditches paralleling the railway there were only 3 occasions when surface water was present. These occurred 178, 209 to 210 and 219 to 220 days after application, on which occasions all herbicides were below the detection limits of between 0.1 and 0.02 μgL^{-1} .

- iii. In the local groundwater, with the exception of two individual samples ($0.08 \mu\text{gL}^{-1}$ imazapyr and $0.1 \mu\text{gL}^{-1}$ oxadiazon out of 58 and 38 samples analysed, respectively), there were no occasions when any of the herbicides applied to the railway were present above the limits of detection. It is likely that the single occurrences of imazapyr and oxadiazon are both 'false positive' detections.
- iv. Within the main stream linked to the railway drainage ditches, atrazine, oxadiazon, oryzalin, imazapyr and isoxaben were never present above the limits of detection. Glyphosate was detected in the stream 'control' samples at a concentration of $0.13 \mu\text{gL}^{-1}$ and diuron was detected on a number of occasions at concentrations ranging from 0.03 to $0.68 \mu\text{gL}^{-1}$. None of these detections were attributed to application to the test railway site as they occurred either before compounds had been applied (glyphosate) or when the drainage ditches adjacent to the railway either did not contain water or showed concentrations below the limit of detection (diuron).
- v. It appears that, for this study, there was no significant leaching of any of the herbicides applied to railway track either to surface-waters or to local ground-waters. This may be because of a combination of degradation and slow recharge related to the specific weather conditions during the study period.

A1.7 Herbicide partitioning to concrete, asphalt and railway ballast (Ramwell, 2002).

This study was undertaken to develop a method suitable for quantifying the sorption of different herbicides to concrete, asphalt and granite ballast and to subsequently determine the partition coefficients for a range of compounds. The method developed was based on the principles of the OECD guidelines for adsorption/desorption. The wearing courses of representative hard surfaces were exposed to a solution of the compound in question, typically at the equivalent label-application rate. Partition coefficients were determined after 144 hours and values were determined for fluoranthene, phenanthrene, atrazine, diuron, oryzalin, isoxaben, isoproturon and dichlorophen on asphalt and concrete and for fluoranthene, phenanthrene, atrazine, diuron on granite ballast. The study concluded that:

- i. The experimental protocol is suitable for determining the partitioning of organic compounds to asphalt and concrete as a standard test and does not require any specialist equipment. Likewise, the proposed environmental constraints of the study are not practically restrictive.
- ii. The majority of herbicide available for removal is lost within the first hour of being exposed to water.

- iii. Herbicides will partition to asphalt and, with the exception of glyphosate, there is an exponential relationship between the K_{oc} of a compound and the K_p for asphalt.
- iv. Herbicide partitioning to concrete is very limited. Again, with the exception of glyphosate, there is an exponential relationship between K_{oc} of a compound and the K_p for concrete. However this relationship is much weaker than for asphalt.
- v. There was no significant partitioning of herbicides to granite ballast.
- vi. Differences between % herbicide losses measured during the current 'desorption' study and those measured during the controlled wash-off study (see section 2.4 above), suggest that physical retention within surface depressions on asphalt and, to a lesser extent on concrete, are a significant factor determining wash-off losses from these surfaces.
- vii. The measured K_p are valuable data for improving the performance of the Tier-1 hard surfaces risk assessment model.

A1.8 Summary of study results and their implications for model development.

The results from the various projects summarised above provide a basis on which to develop the first-tier exposure model. The important conclusions are summarised below and are categorised into those that provide information on: the impacts of rainfall and weather patterns; the influence of catchment characteristics; the mechanisms affecting wash-off from individual surfaces.

A1.8.1 The impact of rainfall and weather patterns

- Very small amounts of rainfall (0.15 to 0.25 mm) initiate run-off and removal of herbicides from concrete and asphalt surfaces (see section 1.4). Within small hard surface catchments (about 100 to 1000 m²) as little as 0.4 to 0.8 mm of rainfall can initiate drainage to receiving ditches, (see sections 1.2 and 1.5).
- For concrete and asphalt surfaces, greatest herbicide losses occur in the first 5 to 7 mm of accumulated rainfall (see sections 1.2 and 1.4).
- For urban and road catchments, small losses of all compounds continue up to at least 58 mm of accumulated rainfall (see section 1.5) or at least 24 days after application (see section 1.2). For railway catchments small losses continue up to 154 mm of accumulated rainfall and 81 days after application (see section 1.3).
- The effect of the timing of rainfall in relation to herbicide application is unclear. Results from the controlled wash-off study (see section 1.4) suggest that, for all types of surface, the magnitude and pattern of wash-off concentrations and % losses are not significantly different for time lags of up to 7 days after application. However results from the roadside

study (see section 1.2) suggested that, for atrazine at least, there were significant differences in the magnitude and pattern of wash-off concentrations and % losses between the study where rainfall initiated run-off the day after application and the study where run-off was not initiated until 9 days after application. This implies that degradation of applied herbicide compounds does not occur on freshly made hard surfaces (as used in the controlled wash-off study), but that, once exposed and weathered in ‘real world’ environments, hard surfaces are likely to acquire some potential for microbial degradation.

- For railway environments, weather patterns influencing the rate of leaching flux through the formation, appear to significantly affect the concentrations of herbicide leachate impacting on local ground-waters (see sections 1.6 and 1.3). It is likely that slow leachate fluxes result in significant dispersion and degradation of any herbicide solute.

A1.8.2 The influence of catchment characteristics

- There is significantly more attenuation of compounds leaching through railway formations than there is of the same compounds washed off concrete and /or asphalt surfaces (see sections 1.2, 1.3 and 1.5).
- In urban and road environments, differences in routing and retention of wash-off related to catchment-size significantly affect the timing and magnitude of wash-off losses to surface water (see sections 1.2 and 1.5).
- There is considerable attenuation of run-off concentrations of herbicides within the surface water body. In the catchment study (Ramwell *et al*, 2000), concentrations of oryzalin, atrazine and glyphosate impacting on the stream were reduced by factors of 2, at least 7 and 49 respectively within a distance of approximately 85 m downstream.

A1.8.3 Mechanism affecting wash-off

- Sorption to surfaces is a significant mechanism for asphalt and to a lesser extent for concrete but does not occur on granite railway ballast (see section 1.7). It is possible that limestone ballast may have similar sorption potential to concrete.
- There is a significant exponential relationship between the K_{oc} of a compound and the K_p for asphalt. There is a similar exponential relationship between K_{oc} and the K_p for concrete but it is less significant (see section 1.7).
- Significant amounts of applied compound appear to be ‘retained’ but not sorbed, in surface depressions in asphalt and, to a lesser extent, in concrete (see section 1.7).
- Although the sorption study (see section 1.7) showed that compounds do not sorb to granite ballast, limited statistical analysis of data from the pilot railway study (see section 1.3)

showed that the only significant factor affecting herbicide losses from the railway formation was compound K_{oc} . This suggests that operational railway formations contain significant amounts of organic material that acts as a sorption medium for compounds leaching through the formation.

- Compound solubility is a significant factor affecting wash-off losses from all surfaces (see sections 1.2 and 1.4). However, results from the controlled wash-off study (see section 1.4) suggest that, for asphalt and concrete, incremental volumes of wash-off contain less of the compound than would be the case if all its potentially soluble mass went into solution.
- On concrete, significant amounts of compounds with relatively low solubility appear to be washed-off in a non-soluble form (see section 1.4). Results from the controlled wash-off study (section 1.4) also suggest that the amount of non-soluble material lost in equal increments of run-off decreases over time.

Appendix 2.

Parameterisation of a Railway Track-bed

The aim of this study was to quantify the total organic carbon (TOC) content of railway ballast taken from track-beds of varying ages.

MATERIALS AND METHODS

Seven minor railway lines were identified for sampling (Table A2-1) as it has previously proved impractical to gain access to permanent way. Although the traffic is lighter on minor lines, with the exception of one site (Hilton), the railways were still in use. Four of the lines had had discrete sections of the ballast replaced, so there were differing ages of ballast within a single line. In total, therefore, there were eleven sampling locations.

Table A2-1 Summary of sampling locations

Site	Code	Location	Ballast age (approx. years)	Stone type
Great Central Railways (Nottingham) [†]	G	Gotham, Leicestershire	0.5 25	Granite
Northampton & Lamport Railway	N	Chapel Brampton, Northamptonshire	0.5 15	Granite
Peak Railway	P	Matlock, Derbyshire	4 10	Limestone
Midland Railway Centre	M	Ripley, Derbyshire	0.5	Limestone
Hilton *	H	Derbyshire	20	Granite & limestone
Chasewater Railway	C	Brownhills, West Midlands	3	Granite & limestone
The Battlefield Line	B	Shackerstone, Leicestershire	10 30	Granite

[†]The site of the second field study (Ramwell *et al.*, 2001); * The site of the first field study (Heather *et al.*, 1999)

Sample collection

It was anticipated that there would be relatively high variation in the nature of ballast from the same railway line. For each age of ballast identified on a line three samples were collected using a trowel.

It was not possible to sample from directly between the sleepers for safety reasons and samples were taken approximately 0.5 m from the outside sleeper-edge. General observations on the railway environment, including the depth of relatively clean ballast (no obvious signs of humus-like material), were made. The samples were stored at 4°C on return to the laboratory.

Particle size analysis

Approximately 500 g of samples was added to a pre-weighed foil tin. Samples were oven-dried at 105°C for 24 hours after which they were re-weighed and sieved through meshes sized 20, 6 and 2 mm to give four fractions (> 20 mm, $20 > 6$ mm, $6 > 2$ mm and < 2 mm). Each fraction was weighed to obtain the percentage each fraction contributed to the whole.

Organic carbon content

It was not possible to weigh samples to exactly the same quantity due to their stoniness and the fact that use of the fines to adjust the weight would give an unrepresentative sample, thus between 500 – 600 g of ballast was weighed out. A visual assessment of the cleanliness of the ballast was made using the classes: very dirty, dirty, moderately dirty and clean. The sample was initially washed in 250 ml of distilled water for 1 min and the washings poured through a 2 mm sieve into a 1 L HDPE bottle. Sample remaining on the sieve was returned to the tin and a further 250 ml of distilled water was added to the sample which was then placed on a Vibramax 100 shaker at speed 2 (circular vibrating) for 10 minutes. The washings were sieved into the same bottle as the first washing. This procedure was repeated a further two times, after which the ballast was visually clean (Figure A2-1). The sieve was rinsed with distilled water between samples. For samples that were notably dirty, a further 500 ml of rinsing water was used and the washing volumes were reduced to 200 ml per wash. The total volume of water used was recorded.

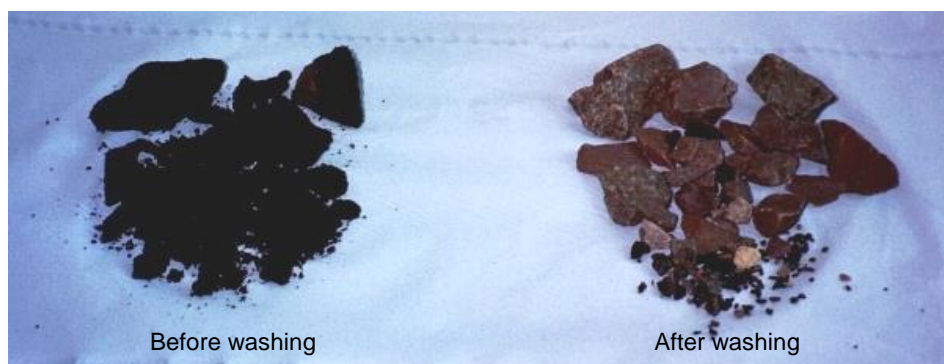


Fig. A2-1 A ballast sample before and after cleaning

In addition to the used railway ballast, new and washed ballast were included to serve as controls, where new ballast was as delivered from the quarry (dust-covered) and washed ballast was new

ballast that has been cleaned in water. This is distinct from ‘clean’ ballast which refers to used ballast collected from the field that contains no visual signs of organic matter.

The bulked washings were stored at 4°C prior to dispatch to TES Bretby, Burton-on-Trent for analysis. Total organic carbon (TOC) of the water fraction was determined by uv-persulphate oxidation with infra-red detection (detection limit = 0.1 mg L⁻¹). TOC of the fines was determined by carbonate removal with sulphurous acid combustion at 800°C with non-dispersive infra-red detection (detection limit = 0.01%). The proportion of fines in the washings was determined to calculate the TOC of the entire sample (water + fines). To account for the different starting weights of each sample, the TOC per kilogram of ballast was calculated.

RESULTS

The total organic carbon for each sampling location is given in Figure A2-2. Sample locations are abbreviated (see Table A2-2) and the approximate age of the ballast is noted. For example, G 0.5 and G 20 indicates samples taken at Gotham from ballast that had been down 6 months and ballast taken from the field study site that had been down approximately 20 years.

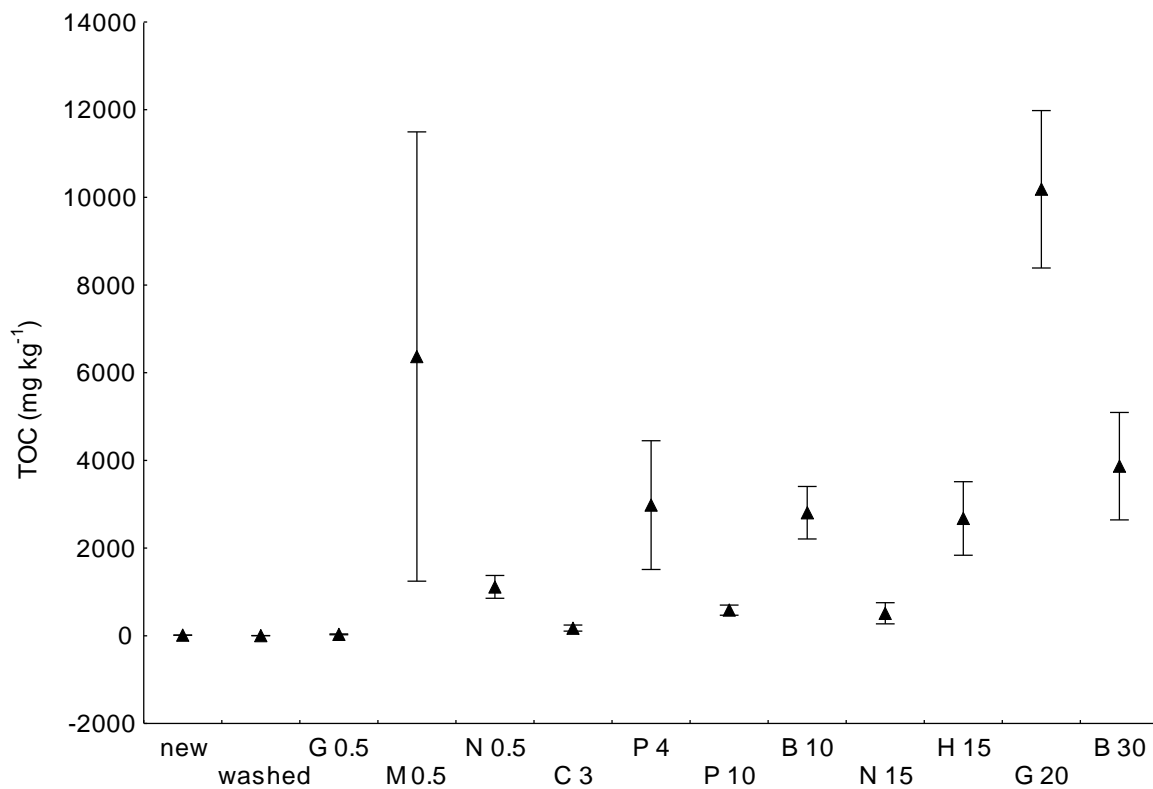


Fig. A2-2 Mean (± S.E.) total organic carbon for railway ballast. Samples are ranked L to R with increasing age

Washed ballast was reported as containing 5.2 mg kg⁻¹ TOC whereas new ballast contained 14.1 mg kg⁻¹ TOC. Whilst ballast older than 0.5 years tended to have higher organic carbon content there were several anomalies. For example, one of the replicates at the Midland Railway Centre that was purportedly 6 months old contained very high quantities of organic carbon (16 g kg⁻¹). On the Peak Railway Line in Matlock, less organic carbon was found in ballast aged approximately 10 years compared to ballast aged *c.* 4 years.

When visually assessing the cleanliness of the ballast, 27% of the individual replicates were described as clean, 45% were moderately dirty whilst the remainder were dirty or very dirty (Figure A2-3).

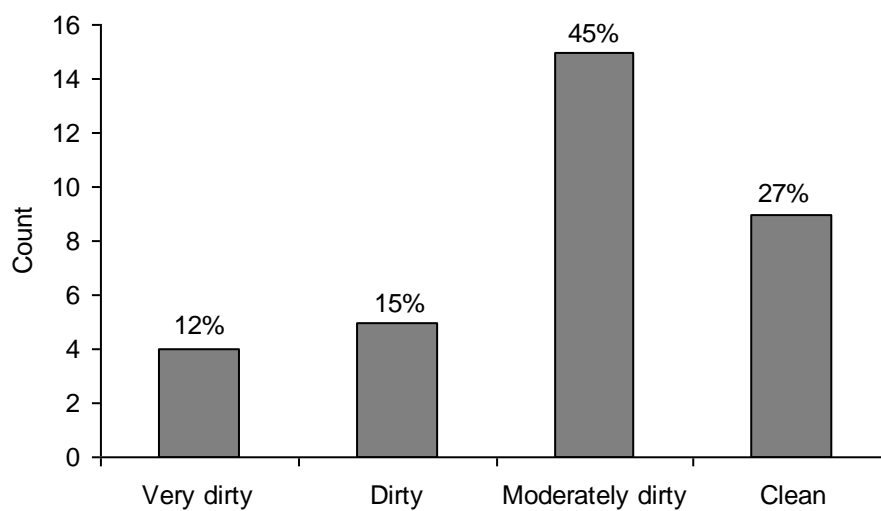


Fig. A2-3 Frequency distribution for the visual assessment of the cleanliness of ballast.

To gain an overview of the distribution of particle sizes, the mean value per sampling site for each particle size as a proportion of the total is illustrated in Figure A2-4. The ballast samples largely consisted of particles greater than 20 mm in diameter; the nominal size of new railway ballast is *c.* 50 mm. In general, older ballast had the greatest number of particles <20 mm, but there were anomalies. There tended to be a higher proportion of particles less than 2 mm in diameter than between 2 and 6 mm. There was variation between replicates within each sampling site. This variation is illustrated for the fine (< 2 mm) fraction in Figure A2-5.

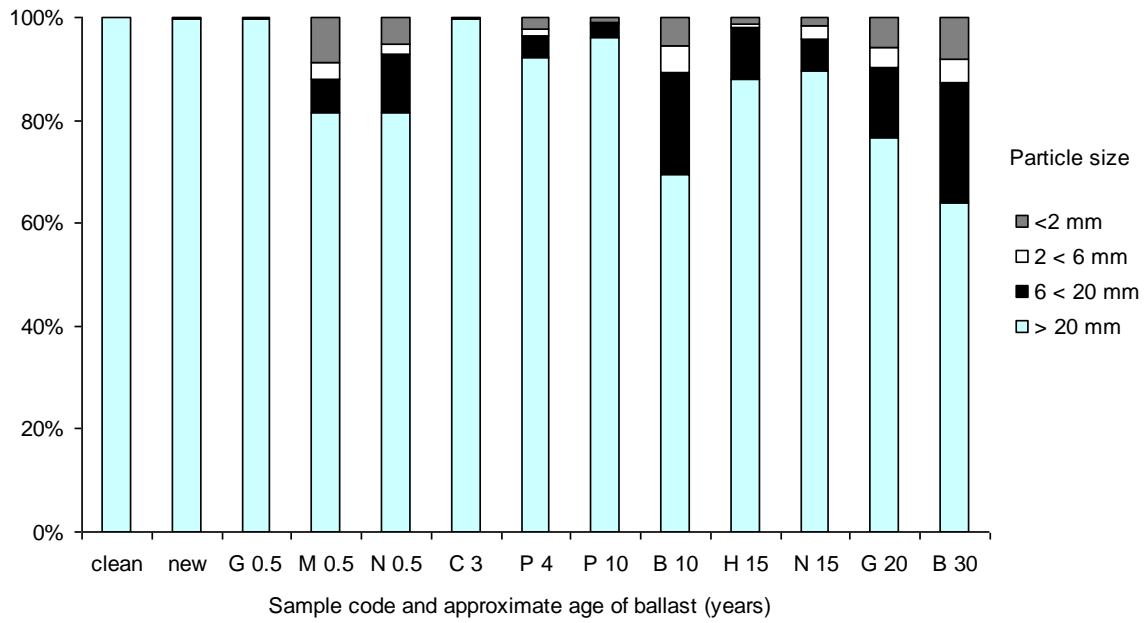


Fig. A2-4 Distribution of particle sizes – mean values per sampling site.

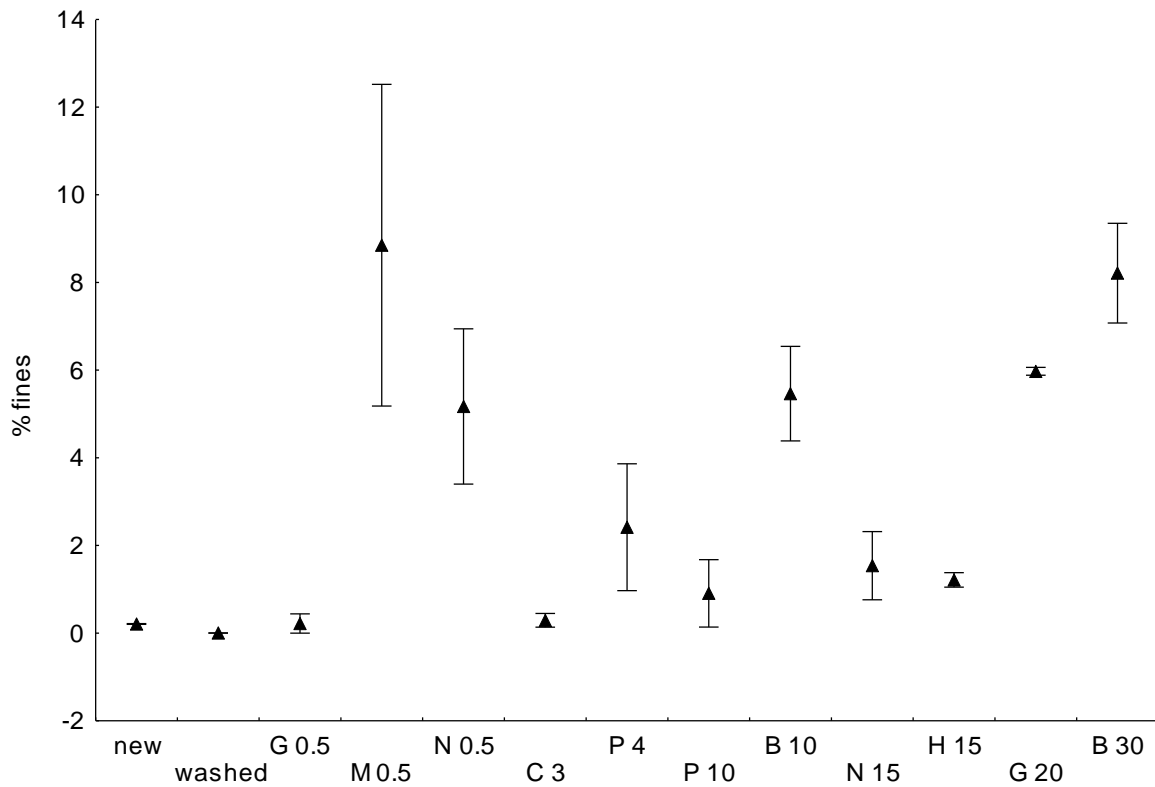


Fig. A2-5 Variation within a sampling site of the fine fraction showing the mean and ± 1 S.E. Samples are ranked L to R with increasing age

General observations of the trackbed

At all railway lines visited there was a clear distinction between a stratum of relatively clean ballast laid on a lower, dirty, humus-containing ballast. This is clearly illustrated in the picture below (Figure A2-6). In general, the depth of the 'clean' ballast varied between 15 and 30 cm, but a depth of 40 cm was noted at one site (Peak Railway). At Chasewater and Northampton the ballast was laid on top of a geomembrane which itself was placed on top of old, dirty ballast.

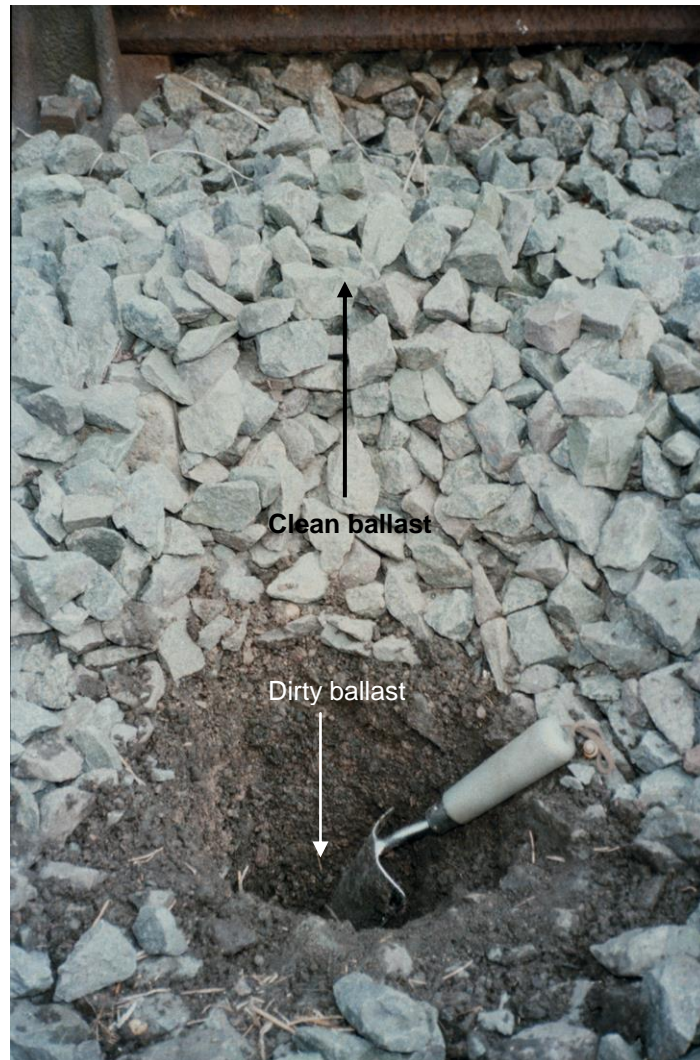


Fig. A2-6 Example of the clear distinction between clean and dirty ballast on a railway track

DISCUSSION

The organic carbon content of railway ballast varied widely between and within sites. Furthermore, although there was a general trend for older ballast to have higher organic carbon content, there were

exceptions and it was not possible to define a relationship between ballast age and OC content. This may be partly due to the fact that the ages of ballast given were only approximate and for some there was an error of ± 5 years. Furthermore, the depth of the working ballast differed between sites and the underlying, 'dirty' ballast that could be included in a sample was of an undetermined age. Consequently, the age of the ballast was not always an accurate indicator of its condition. Furthermore, on permanent way, the condition of railway ballast will be more heavily influenced by factors such as the frequency of use and the speed of traffic which could artificially 'age' the ballast. For these reasons, the quantity of fines is commonly used as an indicator of the condition of ballast and it is normally considered to be spent when 10% of the total mass consists of fines (Clark *et al.*, 2001).

In the current study, there was no statistical relationship between the quantity of fines and the age of the ballast probably for the same reasons that there was no relationship between TOC and ballast age. The quantity of fines (mean values) from each location varied from 0.22% - 8.9% (Figure A2-5), thus the samples were representative of the range of conditions (new – nearly spent) that could be expected to be found in permanent way. In light of the above findings, it would be more appropriate to relate TOC to the condition of ballast, as defined by the quantity of fines, rather than the number of years it has been laid down, *i.e.* its age. Although there was no significant relationship between TOC and the quantity of fines, this may partly be due to the fact that even when ballast was relatively clean, it contained rock dust which would contribute to the fine fraction but not to the OC content. It is suggested therefore that the ballast condition is determined by considering the quantity of fines coupled with a visual assessment of its cleanliness.

In the context of herbicide leaching, although the 'clean' ballast was devoid of obvious organic matter, some herbicide retention could be expected to occur. It is probable that the degree of retention would be similar to that observed in the controlled washoff study (Shepherd and Heather, 1999) because both new ballast and the field ballast visually assessed as clean contained mean fine fractions of 0.2%, and, although the mean TOC of new ballast (14.1 mg kg^{-1}) is less than that of the 'clean' field ballast (mean = 107.5 mg kg^{-1}), the depth of ballast used in the controlled washoff study (40 cm) was approximately double that of the mean field depth (21 cm). The range in depths of clean ballast encountered in the field (mean per location = 15 – 30 cm) were representative of permanent way where recommended ballast depths range from 15 – 28 cm depending on the line speed and tonnage (Cope, 1996).

It is probable that herbicides would be retained to a greater extent in the underlying, dirty sub-ballast where the TOC ranged from 158 – 16535 mg kg^{-1} which equates to 0.02 – 1.7%. The mean organic carbon content for the visually dirty ballast was 0.4%. This compares to 1.18% for vertisols and 1.8% for alfisols (Brady, 1990). However, the reported values of TOC of the visually dirty ballast

may underestimate the OC component of sub-ballast on permanent way because samples analysed were representative of the top 40 cm of ballast which could include some clean ballast. In underestimating the OC content of the sub-ballast, the precautionary principle is encompassed. In addition, it is acknowledged that quantification of total organic carbon will necessarily include carbon from sources such as fly ash which is ordinarily described as inert or black carbon. However, black carbon may exhibit a high affinity for hydrophobic organic compounds (Wu *et al.*, 1999), thus, in terms of herbicide leaching, it may not be accurate to describe black carbon as inert. Consequently, the quantification of the total organic carbon remains a fair descriptor of the potential of ballast to retain herbicides.

The depth of the sub-ballast layer at the sites visited could not be determined during the sampling program as the degree of disturbance to the ballast would have been unacceptable. However, using the findings from a field study (Heather *et al.*, 1999) where the depth to the blanket was circa 70 cm, and considering that, on permanent way the total depth of ballast is circa 60 cm, the depth of 'dirty' ballast could be expected to be in the order of 40 cm.

The findings of the current study may partly explain the results of the two previous field studies conducted at Hilton and Gotham (Heather *et al.* 1999; Ramwell *et al.*, 2001). Herbicides applied to the track at Hilton were detected above $0.1 \mu\text{g L}^{-1}$ in drainage water for a period of several weeks following rainfall events whereas there was no detection of herbicides in either surface or groundwaters at Gotham. The mean TOC contents for the sites were 0.27 and 1.0 mg kg^{-1} respectively, thus the potential for herbicide sorption at Gotham was far greater than at Hilton.

CONCLUSIONS

There was variation in TOC content within and between locations

- There was no relationship between TOC content and the age of the ballast.
- The quantity of fines may be the most appropriate descriptor of the condition of ballast.
- When the fines content is 10% the ballast is considered spent.
- In terms of the quantity of fines, the ballast sampled was representative of the range of conditions that could be expected to exist on permanent way.
- There were two distinct strata of ballast – an upper, relatively clean layer overlying a visually dirty layer containing organic matter.
- The mean organic carbon content of clean ballast (0.01%) was an order of magnitude lower than that of the dirty ballast (0.4%)

- The results provide real data to support the development of a herbicide leaching model.

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The Shackerstone Railway Society, Shackerstone

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Chasewater Railway, Brownhills

Midland Railway Centre, Ripley

Derbyshire County Council

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GLOSSARY OF RAILWAY TERMINOLOGY

There are several terms that have specific meanings when used in the context of the railway environment. These terms are defined below and pictorially represented in Figure A2-7 (all from Cope, 1996).

1. Trackbed

This comprises the ballast and sub-ballast layers including any geomembrane for separating, drainage or strengthening of those layers.

2. Subgrade

This is the term for the natural stratum (soil or rock) or embankment soil after trimming on which the trackbed is constructed.

3. Formation

The term formation is often used to refer indiscriminately to either ballast or subgrade, or sometimes the interface between them. However, if the term is used it should be synonymous with subgrade.

4. Blanket

A blanket is a permeable layer of fine, granular material placed directly on cohesive subgrade. A blanket is not necessary if the subgrade is non cohesive.

5. Permanent Way

Permanent Way refers to the main railway lines used by the public that are under the jurisdiction of, what was previously, Railtrack.

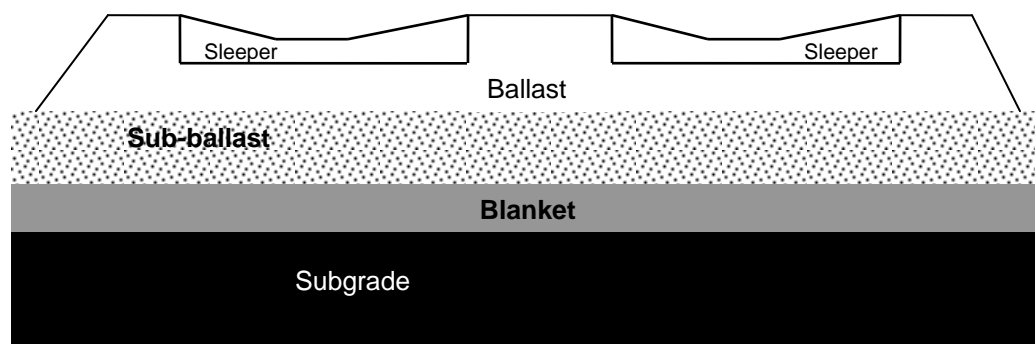


Figure A2-7 Diagrammatic representation of a railway line

Appendix 3.

Calibration of the surface wash-off and ballast leaching sub-models.

The following Appendix gives a detailed description of the process steps incorporated into the surface wash-off models and the ballast leaching model, together with the equations used to simulate those processes and the calibration of parameters incorporated into the equations. Summary descriptions of the model process steps are given in sections 3.1.2 of the main report.

A3.1 THE SURFACE WASH-OFF SUB-MODEL

The Surface wash-off sub-model incorporates the following steps:

Step 1

When the applied herbicide compound reaches a specific type of hard surface, some of it is absorbed and some is sorbed to that surface. At this stage the amounts that are absorbed and sorbed are not specified in the model.

Step 2

During the first wash-off step of the model, which is equivalent to the first 0.25 L of run-off per 0.54 m² of surface, rainfall accumulates on the surface, interacts with the compound and washes off some soluble and some non-soluble masses depending on compound solubility, compound specific gravity and surface-specific characteristics of retention and sorption.

2a. Calculation of the volume of water involved in the first wash-off step

The water volume involved in the first volume step is the run-off volume (0.25L) plus the volume of water retained on the surface before (and after) wash-off is initiated. This volume is derived from measurements taken during the controlled wash-off study (Shepherd & Heather, 1999) and is surface-specific: 0.138L per 0.54 m² for asphalt and 0.073 L per 0.54 m² for concrete. The volume of water involved in the first wash-off step is thus:

For asphalt surfaces: 0.388

For concrete surfaces: 0.323

2b. Calculation of the mass of compound lost in solution during the first wash-off step

During the first wash-off step of each rainfall event, the mass of compound applied that goes into solution depends on the volume of water in the step and the solubility of the compound, although for very soluble compounds, the amount going into solution obviously cannot exceed the amount of compound on the surface that interacts with incident rain. However, the controlled wash-off study (Shepherd & Heather, 1999) indicated that, on asphalt, not all of the compound that could potentially go into solution during the first 0.25 L of wash-off (based on the compound solubility & the run-off volume) is actually lost in that run-off. This observation was made from the results for glyphosate which has a solubility so large (116,000 mg L⁻¹) that all the applied mass that is not sorbed should go into solution in the first 0.25 L of run-off. This was not the case and the fraction of applied mass that was lost was therefore calculated from:

$$\frac{\text{Measured mass of glyphosate lost from asphalt in the first 250 ml of wash-off}}{(\text{Mass of glyphosate applied} - \text{mass sorbed})}$$

Where the mass sorbed is calculated from the surface-specific K_p for glyphosate and the volume of water involved in the first step. It should be noted that, for glyphosate K_{p_{asphalt}} is 0 and thus none is sorbed onto the surface.

This calculation gave a value of 0.3507 indicating that, on asphalt, only about 1/3 of all the potentially soluble amount in the first 0.25 L of run-off is actually lost in that run-off, meaning that the remaining 2/3 is actually 'lost' back onto the asphalt surface in some way.

Similar calculations for glyphosate on concrete surfaces using the measured surface-specific K_p of 10.21, gave a value of ~1 indicating that all of the 0.25 L of run-off water moving over the concrete surface is able to form solute with the available mass, probably because the concrete surface is much smoother than that of asphalt and none of the solute run-off is 'lost' during transport over its surface.

Based on this calibration, the amount of compound that is lost as solute during the first wash-off step is:

Equation 1

For asphalt surfaces: EITHER: $0.25 * \text{compound solubility} * 0.3507 \text{ (mg L}^{-1}\text{)}$, OR:
 $\text{Mass applied} * 0.3507$. Whichever is the smaller value.

For concrete surfaces: EITHER: $0.25 * \text{compound solubility (mg L}^{-1}\text{)}$, OR:
 Mass applied . Whichever is the smaller value.

The second option for each surface is required to ensure that, for very soluble compounds, the mass that goes into solution does not exceed the mass applied.

2c. Calculation of the mass of compound sorbed during the first wash-off step

For very soluble compounds, where the potentially soluble material in the volume of water in the first wash-off step exceeds the mass on the surface, then all of this mass is available for equilibration sorption. For such compounds, the mass sorbed is simply calculated from:

Equation 2

For asphalt surfaces: IF (solubility \times 0.388) \geq mass reaching the surface,

THEN:

$$\text{sorbed mass} = \text{Mass reaching the asphalt surface} \times (1 - (0.388 / (0.388 + (0.54 \times K_p \text{ asphalt}))))$$

For concrete surfaces: IF (solubility \times 0.323) \geq mass reaching the surface,

THEN:

$$\text{sorbed mass} = \text{Mass reaching the concrete surface} \times (1 - (0.323 / (0.323 + (0.54 \times K_p \text{ concrete}))))$$

For less soluble compounds however, only the potentially soluble mass plus a fraction of the remaining mass is available for sorption. The inability of all of the remaining (non-soluble) mass to participate in sorption equilibration is indicated by examining the measured mass of isoxaben lost from concrete in the first 250 mL of runoff from the controlled wash-off study. If this mass is added to the theoretical sorbed mass of isoxaben (based on the measured K_p value of 1.62), assuming all the applied compound that is not in solution was available for equilibration sorption, then the sum is almost 0.5 mg in excess of the 4 mg applied to the concrete surface. It thus appears that not all of the non-soluble mass remaining on the surface participates in sorption, probably because the weak ionic nature of such compounds means that some of the mass is too far away from the hard surface to be attracted to it.

Derivation of the fraction of non-soluble mass that is not available for equilibration sorption was by calibration and the derived value is 0.18 for asphalt and 0.355 for concrete surfaces. These values gave the best overall fit to the measured masses of isoxaben, oryzalin, diuron and atrazine lost in the first 250 ml of runoff collected during the controlled wash-off study. The difference in the values probably relate to differences in surface area, asphalt having a much greater surface area than concrete because of its greater surface roughness. This means that compound on the surface of asphalt is spread out 'thinner' than an equivalent amount on the surface of concrete.

Using this calibration, for those compounds where the mass of soluble material in the volume of water in the first wash-off step is less than the mass on the surface, the amount of compound sorbed/absorbed per 0.54 m² of hard surface during the first wash-off step is calculated as follows:

Equation 3

For asphalt surfaces: IF (solubility x 0.388) < mass reaching the surface,

THEN:

$$\text{sorbed mass} = \left[\left[\text{Mass reaching the asphalt surface} - (\text{solubility} \times 0.388) \right] \times 0.82 \right] + (\text{solubility} \times 0.388) \times \left(1 - \left(0.388 / (0.388 + (0.54 \times K_p \text{ asphalt})) \right) \right),$$

For concrete surfaces: IF (solubility x 0.323) < mass reaching the surface,

THEN:

$$\text{sorbed mass} = \left[\left[\text{Mass reaching the concrete surface} - (\text{solubility} \times 0.323) \right] \times 0.645 \right] + (\text{solubility} \times 0.323) \times \left(1 - \left(0.323 / (0.323 + (0.54 \times K_p \text{ concrete})) \right) \right),$$

2d. Calculation of the non-soluble mass of compound washed off each surface during first wash-off step

For less soluble compounds, water movement over the surface also physically interacts with the non-sorbed mass that does not go into solution, detaches some of it and transports it off the surface in non-soluble form. The amount of available mass transported in this way is dependent on the surface type and is also dependent on the compound specific gravity. Much more of a specific compound is transported in non-soluble form over concrete than over asphalt because concrete has a much smoother surface than asphalt and less energy is thus required to transport non-soluble material over its surface. Similarly compounds with a relatively large specific gravity are denser than those with a smaller specific gravity and thus require greater energy to transport equivalent amounts of compound.

For **concrete surfaces**, a strong relationship between compound specific gravity and the fraction of available mass washed off in non-soluble form was derived using data from the controlled wash-off study. Firstly, non-soluble losses of atrazine, diuron, oryzalin and isoxaben were calculated from the measured data as follows:

Measured mass lost in the first 0.25 L of wash-off - Calculated soluble mass lost as specified in step 2d above.

These values were then expressed as a fraction of the non-sorbed mass and used to derive the following ‘best-fit’ relationship with compound specific gravity:

Equation 5

Fraction of non-sorbed mass lost in non-soluble form in first 0.25 L of wash-off from concrete = 0.9407 - (0.5839 x compound specific gravity).

A comparison of the fractions calculated from the measured data and the fractions estimated from the fitted relationship with specific gravity is shown in Fig. A3.1-1. The correlation coefficient (r^2)

of 0.9937 between the two sets of values shows that the specific gravity relationship gives a very good prediction of the fraction derived from the measured data.

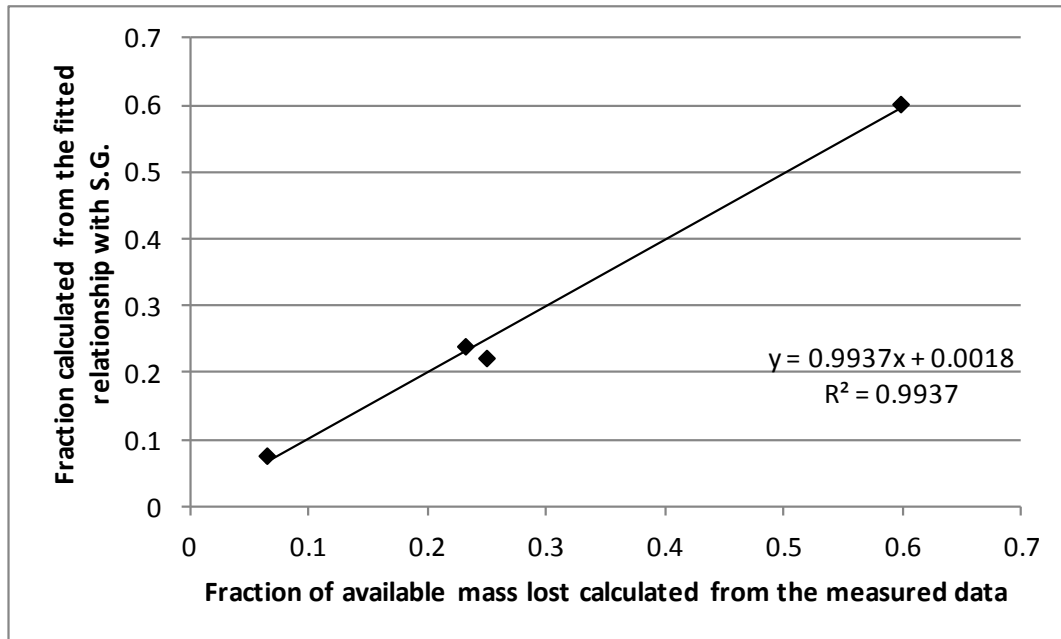


Figure A3.1-1 Relationship between compound losses from concrete in non-soluble form, expressed as a fraction of the available non-sorbed mass, calculated from measured data for atrazine, diuron, oryzalin & isoxaben and estimated from the derived relationship with specific gravity.

However, although the derived specific gravity relationship provides a good fit with the fractions estimated from the measured data, it does not necessarily give reasonable prediction for compounds with specific gravities outside the range studied. In particular, for compounds with specific gravity above about 1.6 the predicted fraction would be negative. It is thus necessary to put some bounds on the relationship and this was achieved by assuming that it has a form in which the fraction is 1 at a specific gravity of 0 and effectively 0 at a specific gravity of 2.5.

This relationship was achieved by extrapolating the linear relationship to a specific gravity of 0.4 and then fitting an exponential decay relationship for the specific gravity ranges from 0.4 to 0 and from 1.48 to 2.5. The resulting curves are shown in figure A3.1-2 and the equations for the power and exponential decay relationships are:

Equation 6

IF compound specific gravity <0.4, then the fraction of non-sorbed mass lost in non-soluble form = EXP(-0.986462 x S.G.).

IF compound specific gravity >1.48, then the fraction of non-sorbed mass lost in non-soluble form = 589.4 x EXP(-6 x S.G.).

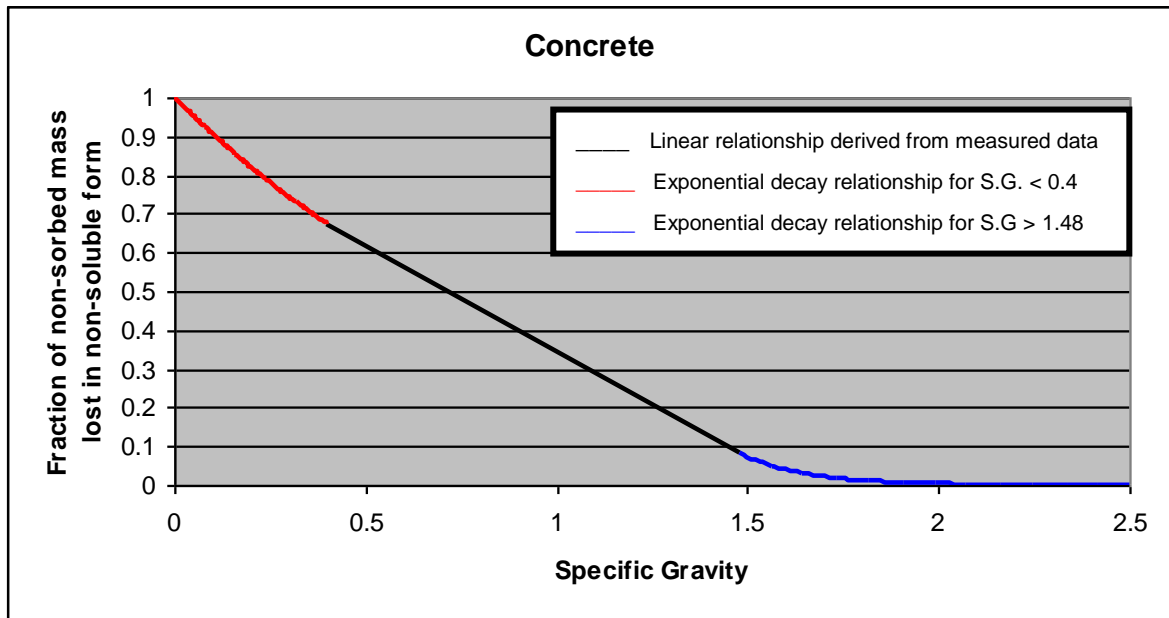


Figure A3.1-2 Extrapolated predictive relationship between compound specific gravity and the fraction of non-sorbed mass available for interaction lost in non-soluble form in the first 0.25 L of wash-off from concrete.

For **asphalt surfaces**, the fractions of available mass washed off in non-soluble form calculated from the measured data for atrazine, diuron, oryzalin and isoxaben are shown in table A3.1-1, together with the compound specific gravity.

Table A3.1-1. Specific gravity of atrazine, diuron, oryzalin & isoxaben compared to the fraction of non-sorbed mass lost in non-soluble form in the first 0.25 L of wash-off from asphalt, calculated from measured data (Shepherd & Heather, 1999).

Compound	Specific Gravity	Calculated fraction of non-sorbed mass lost in non-soluble form
atrazine	1.23	0.0052
diuron	1.48	0.0061
oryzalin	1.2	0.0042
isoxaben	0.58	0

The calculated values are two orders of magnitude smaller than those on concrete and show little relationship with compound specific gravity. In fact, any trend with specific gravity appears to be a positive one with smaller fractions associated with smaller specific gravity values. Such a relationship is the opposite of that derived for concrete surfaces and is difficult to justify mechanistically. On asphalt surfaces therefore compound losses in non-soluble form appear to be very small and it is difficult to derive a robust calibration of the mechanism for them. This is

probably because, on asphalt, large amounts of the non-sorbed compound appear to be isolated in surface crevices (see section 2b above) and water moving over the surface does not have enough energy to detach and move significant amounts of such material. Nevertheless, in mechanistic terms, compound specific gravity should influence the relative amounts of non-soluble losses from asphalt in the same way as it does for concrete. A ‘best fit’ linear relationship between specific gravity and the fraction of non-sorbed compound lost in non-soluble form was thus derived for asphalt to match that derived for concrete surfaces. This relationship is as follows:

Equation 7

$$\text{Fraction of non-sorbed mass lost in non-soluble form in first 0.25 L of wash-off from asphalt} = 0.005 - (0.00005 \times \text{compound specific gravity}).$$

The slope of the relationship is almost level, because of the over-riding influence of retention on the asphalt surface. However, in order to maintain consistency of the mechanisms within the model, it is still necessary to extrapolate the derived relationship to the bounds previously specified for concrete. For larger specific gravities, this was done by extrapolating the linear relationship derived for asphalt by increasing the specific gravity to a point where the line crosses that of the exponential decay relationship derived for concrete and then using that exponential decay relationship to decrease the fraction to 0. The value of specific gravity at which the two lines cross is 1.9495 and this was thus set as the upper bound for the linear relationship derived for asphalt. For smaller specific gravities, a power decay relationship was fitted to derive a curve where the fraction for a specific gravity of 0.4 was equal to that of the derived linear relationship and the fraction for a specific gravity of 0 was 1. The resulting equations for the power and exponential decay relationships are given below and the complete curvilinear relationship for asphalt is shown in figure A3.1-3.

Equation 8

$$\text{IF compound specific gravity } < 0.4, \text{ THEN the fraction of non-sorbed mass lost in non-soluble form} = 1 - (S.G.^{0.00544853}).$$

$$\text{IF compound specific gravity } > 1.9495, \text{ THEN the fraction of non-sorbed mass lost in non-soluble form} = 589.4 \times \text{EXP}(-6 \times S.G.).$$

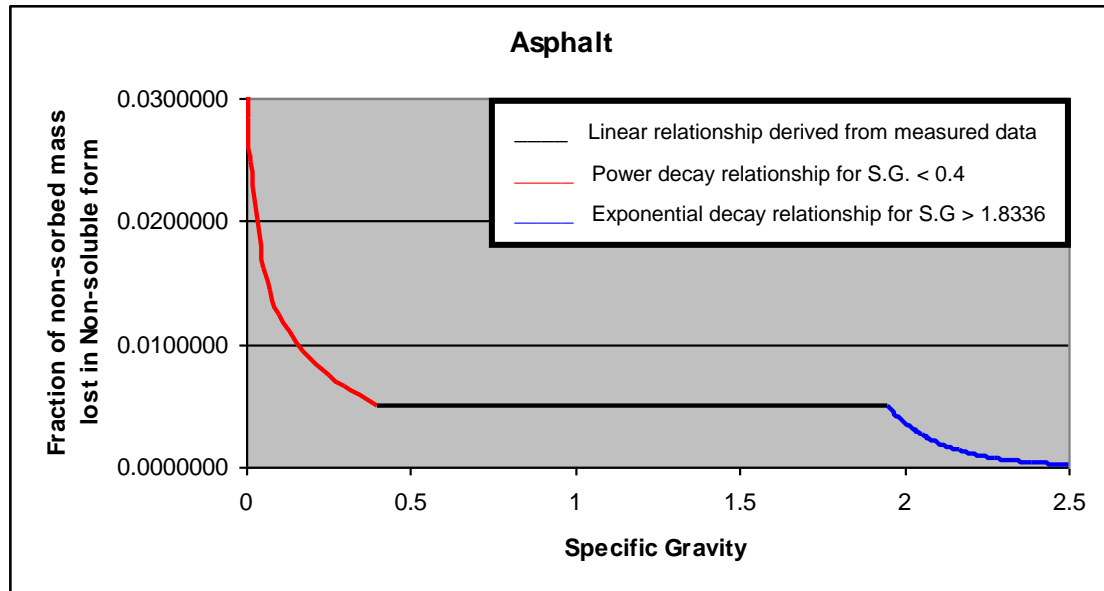


Figure A3.1-3 Extrapolated predictive relationship between compound specific gravity and the fraction of non-sorbed mass available for interaction lost in non-soluble form in the first 0.25 L of wash-off from asphalt.

Step 3

During subsequent wash-off-steps, which are equivalent to each 0.25 L of wash-off per 0.54 m² of surface, water moving over the surface continues to interact with the compound present, washing off some in soluble and some in non-soluble form. As with the first wash-off step, the amounts lost depend on compound solubility, compound specific gravity and surface-specific characteristics of retention and sorption. In subsequent volume-steps however, the amount lost also depends on the amounts remaining in the sorbed and non-sorbed phases at the end of the previous wash-off-step.

3a. Calculation of the mass sorbed during each wash-off-step

During each wash-off-step, the mass of compound sorbed to each surface type is the same as that of the previous step, as long as some compound remains in the non-sorbed phase. As soon as this is not the case, then de-sorption occurs and a new equilibration sorption is calculated for the wash-off-step. However, because water in these steps is moving over the surface relatively quickly, only a fraction of the sorbed compound participates in equilibration. In addition, this fraction successively reduces with each step as the more weakly bound areas of compound are preferentially removed, leaving only the more strongly bound areas of compound. The equation for calculating the mass of compound de-sorbed during each wash-off step is thus

Equation 9

IF mass not sorbed = 0, OR Mass not sorbed < potential soluble mass lost in run-off, THEN

Mass de-sorbed =

For asphalt surfaces:

(Mass sorbed at start of the wash-off step x de-sorption fraction) - {(Mass sorbed at start of the wash-off-step x de-sorption fraction) x [1 - (0.388/(0.388 + (0.54 x Kp_{surface})))]}

For concrete surfaces:

(Mass sorbed at start of the wash-off step x de-sorption fraction) - {(Mass sorbed at start of the wash-off-step x de-sorption fraction) x [1 - (0.323/(0.323 + (0.54 x Kp_{surface})))]}

The de-sorption fraction depends on the number of wash-off steps since rainfall was initiated and the strength of surface sorption. This function takes the form:

Equation 10

$$\text{De-sorption fraction} = a_{\text{fraction}} \times (n-1)^{-b_{\text{power}}}$$

Where a_{fraction} is the initial fraction value for the power reduction function

n is the wash-off step number for each rainfall event.

b_{power} is the power reduction value applied to n .

As desorption can only ever occur after the initial wash-off step, the wash-off step incremental number is always $n-1$. The values of a and b determine the initial fraction of sorbed compound that is subject to de-sorption and the amount that fraction reduces with each subsequent wash-off step. These values were calibrated using the amounts of wash-off measured in the controlled wash-off study. In the controlled wash of study, it was calculated that de-sorption was only initiated on concrete surfaces and for the compounds isoxaben and glyphosate. For these two compounds the measured mass lost in each successive 0.25 L of wash-off was used to derive a best-fit value for the “ a ” and “ b ” parameters. Because these parameters deal with sorption/desorption it is assumed they are dependent on the surface specific K_p value and are likely to have the following relation with it:

Equation 11

$$\text{“}a_{\text{fraction}}\text{” or “}b_{\text{power}}\text{”} = \text{constant} \times Kp_{\text{surface}}^{\text{(power)}}$$

Using the derived best fit values of “ a ” and “ b ” equation 11 was solved for each one, giving the resulting equations:

Equation 12

$$\begin{aligned} \text{“}a_{\text{fraction}}\text{”} &= 0.7195 \times Kp_{\text{surface}}^{-0.377} \\ \text{“}b_{\text{power}}\text{”} &= 0.6218 \times Kp_{\text{surface}}^{0.2455} \end{aligned}$$

The accuracy of prediction of the calculated fraction using this equation is shown in figure A3.1-4

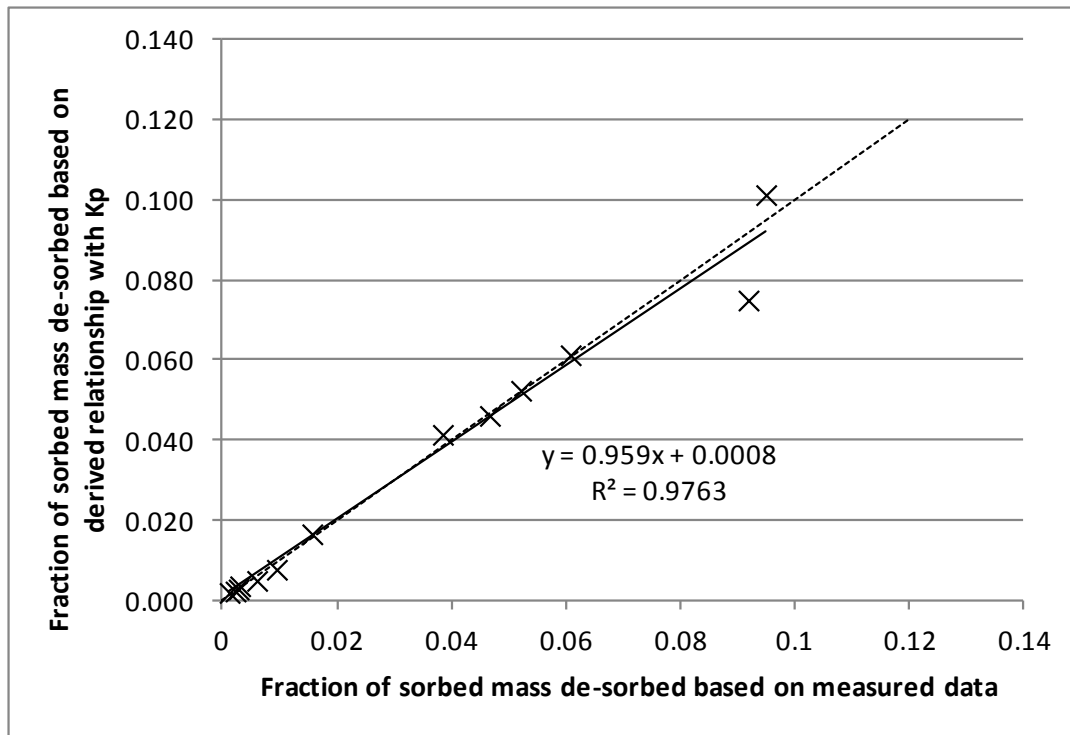


Figure A3.1-4 Accuracy of prediction of the fraction of sorbed mass involved in de-sorption. The thin dotted line represents the 1 : 1 relationship

Substituting equations 11 into equation 9 enables the mass de-sorbed in each wash-off step to be calculated.

For compounds of low solubility however, the mass that de-sorbs into water moving over the surface cannot exceed the solubility of the compound in the volume of water available. It is therefore necessary to impose a restriction on the mass de-sorbed, such that the calculated mass does not exceed a value of:

Equation 13

For asphalt surfaces:

$$\text{Compound solubility (mg L}^{-1}\text{)} \times 0.25 \times 0.3507 \times \text{de-sorption fraction}$$

For concrete surfaces:

$$\text{Compound solubility (mg L}^{-1}\text{)} \times 0.25 \times \text{de-sorption fraction}$$

The actual mass de-sorbed in the wash-off step is the smaller of the two calculated values.

3b. Calculation of the soluble mass of compound washed off each surface during each step

For each wash-off-step, if the mass of non-soluble material that remains at the surface is zero then the only soluble losses that can occur are the result of de-sorption and are calculated as described in step 3a above. As long as some compound remains on the surface in non-soluble form however, water moving over the surface continues to interact with it to form solute. As with the first wash-

off-step, the fractions of wash-off water that interact with compound are different for different surfaces but these fractions successively decrease with each step as the increasing speed of wash-off water reduces the effective volume of interaction between the two. The fraction of wash-off volume involved in the interaction is a function of surface type, the number of steps since wash-off was initiated and compound solubility. The function takes the form:

Equation 14

$$\text{Fraction of effective wash-off volume} = n^{-X_s}$$

Where x_s is a function of surface type and compound solubility.

n is the wash-off step number.

This equation gives a power function decrease in the effective volume of wash-off that can form solute in each succeeding wash-off-step. For each surface, the power function x_s in equation 14 was calculated from the losses of isoxaben, oryzalin, diuron and atrazine measured in the controlled wash-off study (Shepherd & Heather, 1999).

For asphalt, a power function for each compound was derived to give the best-fit shape to the measured total losses over each succeeding volume step. This is because, on asphalt, non-soluble losses form only a very small component of the total losses and thus a function that gives the best-fit shape should equate to the reduction in soluble losses over time. The derived power value, $x_{asphalt}$, for each compound was then related to compound solubility using a best fit curve. The derived relationship is shown in Figure A3.1-6 and enables a value for $x_{asphalt}$ to be derived as follows:

Equation 15

$$x_{asphalt} = 0.8346 \times \text{EXP} (-(0.051 \times \text{solubility}))$$

Derivation of the power function $x_{concrete}$ was slightly different as, on this surface, non-soluble losses form the largest component of wash-off for most compounds and, for isoxaben, the non-soluble pool on the surface is exhausted after the second volume-step. For concrete surfaces therefore, only the measured losses of oryzalin, diuron and atrazine, together with the measured loss of isoxaben in the second wash-off step, were used in the calibration. For each of these compounds, soluble losses in each 0.25 L of wash-off following the first wash-off step were estimated by varying the power values in equations 14 and 18 to give a best-fit to the measured data. The derived power value, $x_{concrete}$, for each compound was then related to compound solubility using a best fit curve. This relationship is shown in Figure A3.1-7 and enables a value for $x_{concrete}$ to be derived as follows:

Equation 16

$$X_{concrete} = 0.7211 - (0.0079 \times \text{solubility})$$

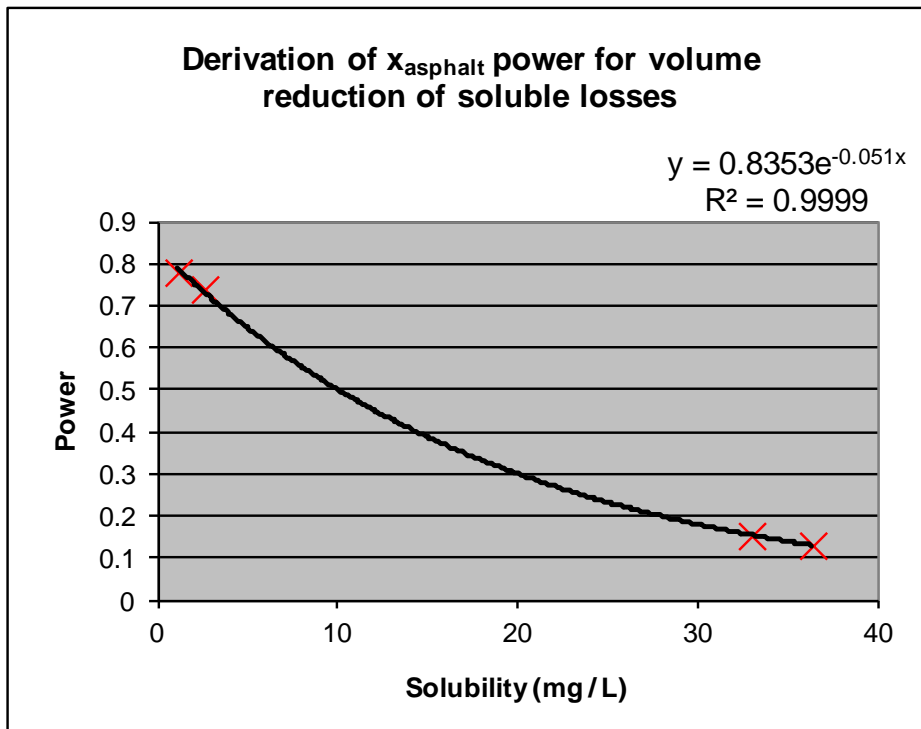


Figure A3.1-5 Derived relationship between specific solubility and the soluble loss power reduction value $x_{asphalt}$ for wash-off volume-steps.

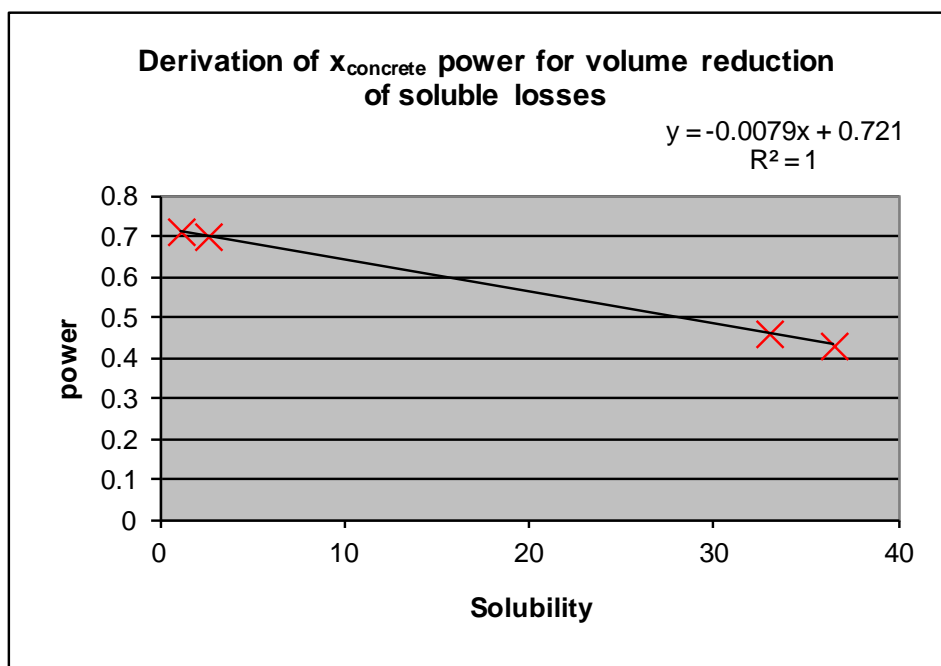


Figure A3.1-6 Derived relationship between specific solubility and the soluble loss power reduction value $x_{concrete}$ for wash-off volume-steps.

The negative relationships with solubility mean that the higher the solubility the smaller the power and thus the larger the fraction derived using equation 14. In other words, for equivalent volume-steps, the more soluble a compound is, the larger are the soluble phase losses.

This type of relationship does not hold for very soluble compounds however. This is because, above a level of solubility where all losses are in soluble form, irrespective of the amount of non-sorbed material present:

- On concrete surfaces, all non-sorbed compound on the surface at the start of rainfall will be washed off in the first wash-off step, after which all wash-off losses are the result of de-sorption processes;
- On asphalt surfaces only 0.3507 of the non-sorbed compound on the surface is available to form solute during the first wash-off step (see 2b above). During subsequent wash-off steps, the power reduction of this fraction is dependent on the level of interaction between the water travelling over the surface and the amount of compound remaining on the surface. Thus, for compounds with small application rates, the area of interaction in relation to the mass applied will be greater than for compounds with larger application rates. Derivation of the power value, $y_{asphalt}$, for such cases was based on measured data from the controlled wash-off studies for glyphosate and an un-named compound (subject of a confidential wash-off study), both of which are extremely soluble but not sorbed to asphalt. For each successive wash-off-step, the measured mass lost was calculated as a fraction of the non-sorbed mass present at the start of that step. This fraction was successively smaller than that for the first was-off step and was assumed to represent a soluble loss reduction factor R applied to it, such that the fraction is $0.3507 \times R$, where R is a reduction factor taking the form:

Equation 17

$$R = n^{-y_{asphalt}}$$

Where n is the wash-off step number for a specific rainfall event.

$y_{asphalt}$ is the power reduction value applied to n .

The power $y_{asphalt}$ depends on the amount of mass applied per 0.54 m² with an assumed power relationship taking the form:

$$y_{asphalt} = c \times m^d$$

Where c is the constant for the mass applied

m is the mass applied per 0.54 m^2 .

d is the power value applied to m .

Best fit values for y_{asphalt} were derived for the two compounds with measured data and equation 17 was solved for these values giving the following equation:

Equation 18

$$y_{\text{asphalt}} = 1.2226 \times m^{0.14}$$

Combining equations 17 and 18 gives the following equation for asphalt

Equation 19

$$\text{Fraction of non-sorbed mass lost} = 0.3507 * [n^{-(1.2226 \times m^{0.14})}]$$

Where n is the wash-off step number.

m is the mass applied per 0.54 m^2

The accuracy of this prediction based on the time step and mass applied is shown in Figure A3-1-7 where the predicted fraction is plotted against the fraction calculated from the measured wash-off data.

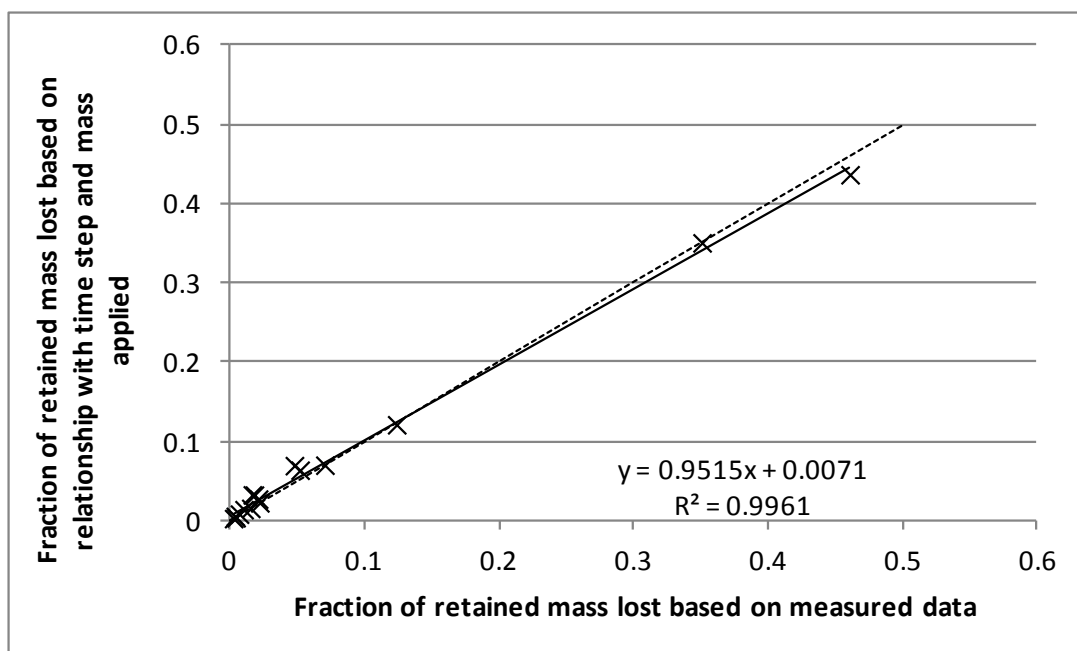


Figure A3.1-7 Accuracy of prediction of the fraction of retained mass on asphalt lost during successive wash-off steps. The thin dotted line represents the 1 : 1 relationship

The calculation of soluble mass lost in each successive wash-off step combines equations 14, 15, 16 and 19 and takes the form:

Equation 20

Soluble mass lost in successive wash-off steps =

For asphalt surfaces:

*EITHER: solubility * 0.25 * 0.3507 * (n^{-(0.8322 x EXP(-(0.0453 x solubility)))})*

*OR: Fraction of non-sorbed mass * 0.3507 * [n^{-(1.2226 x m^{0.14})}]*

Whichever is the smaller value.

For concrete surfaces:

*EITHER: [0.25 * n^{-(0.7211 - (0.0079 x solubility))}] * compound solubility (mg L⁻¹),*

OR: Non-sorbed mass. Whichever is the smaller value.

Where n is the wash-off step number.

As with calculation of soluble losses for the first wash-off-step, the second option for each surface is required to ensure that, for very soluble compounds, the mass lost in solute form does not exceed the mass available for interaction.

One further condition needs to be applied to complete the calculation of soluble losses. This condition is required to prevent the amount of soluble losses calculated using equations 14, 15 and 16 exceeding the amount of non-soluble material present on the surface at the start of the wash-off step. If this is the case, then the actual soluble losses in that step must comprise whatever non-soluble mass is present at the start of the step, plus whatever mass de-sorbs from the surface as water flows over it. Calculation of the amount of de-sorbed mass lost needs to take into account the fact that some of the water flowing over the surface will be interacting with the non-soluble mass to form solute, rather than acting to de-sorb compound from the surface. The amount of de-sorbed mass in such situations is therefore calculated as described in equation 9 (see step 3a above) but is scaled down by subtracting the non-soluble mass that is lost forming solute with the water flowing over the surface from the sorbed mass that then takes part in desorption. Thus:

Equation 21

Mass de-sorbed if calculated soluble loss exceeds the mass of non-soluble compound on the surface

For asphalt surfaces:

{(Mass sorbed at start of the wash-off step-mass lost as solute) x de-sorption fraction} -

[{(Mass sorbed at start of the wash-off step-mass lost as solute) x de-sorption fraction} x [1

- (0.388/(0.388 + (0.54 x K_{p,surface})))]]

For concrete surfaces:

$$\{(\text{Mass sorbed at start of the wash-off step} - \text{mass lost as solute}) \times \text{de-sorption fraction}\} - \left[\{(\text{Mass sorbed at start of the wash-off step} - \text{mass lost as solute}) \times \text{de-sorption fraction}\} \times \left[1 - (0.323 / (0.323 + (0.54 \times K_{p_{\text{surface}}})) \right) \right]$$

3c. Calculation of the non-soluble mass of compound washed off each surface during each wash-off step

For each wash-off step, if the mass of non-soluble material that remains at the surface is zero or is smaller than the calculated soluble losses, no non-soluble phase losses can occur. If this is not the case but the mass of non-soluble material that remains at the surface is smaller than the calculated soluble losses plus non-soluble losses, then the non-soluble loss in the volume-step is calculated as follows:

Equation 22

$$\begin{aligned} & \text{Non-soluble mass lost in the wash-off step} \\ & = \text{Non-soluble mass at the start of the step} - \text{Calculated soluble loss in the wash-off step} \end{aligned}$$

If none of these conditions are met, then sufficient compound remains on the surface in non-sorbed form following solute formation to allow some fraction of it to be detached and removed in wash-off. However, this fraction decreases rapidly with each succeeding volume step because most of the more easily moved material is removed in the initial wash-off and the remaining amount is increasingly difficult to detach. The fraction of non-sorbed material lost in each wash-off step is a function of the number of steps since wash-off was initiated and the compound specific gravity. The function takes the form:

Equation 23

$$\begin{aligned} & \text{Non-soluble phase mass lost in the first } 0.25 \text{ L} \times n^{-z_s} \\ & \text{Where } z_s \text{ is a function of specific gravity and surface type.} \\ & n \text{ is the wash-off step number.} \end{aligned}$$

This equation gives a power function decrease in the non-soluble mass lost in each succeeding step. As for the power function x_{concrete} in equation 14, the power function z_{concrete} in equation 20 was calculated from the measured losses of oryzalin, diuron and atrazine on concrete. For each of these compounds, non-soluble losses in each 0.25 L of wash-off following the first wash-off step were estimated by varying the power values in equations 14 and 21 to give a best-fit to the measured data. The derived power value, z_{concrete} , for each compound was then related to compound specific

gravity using a best-fit curve. The derived relationship is shown in Figure A3.1-9 and enables a value for $z_{concrete}$ to be derived as follows:

Equation 23

$$z_{concrete} = 1.0256 \times \text{Specific Gravity}^{2.3071}$$

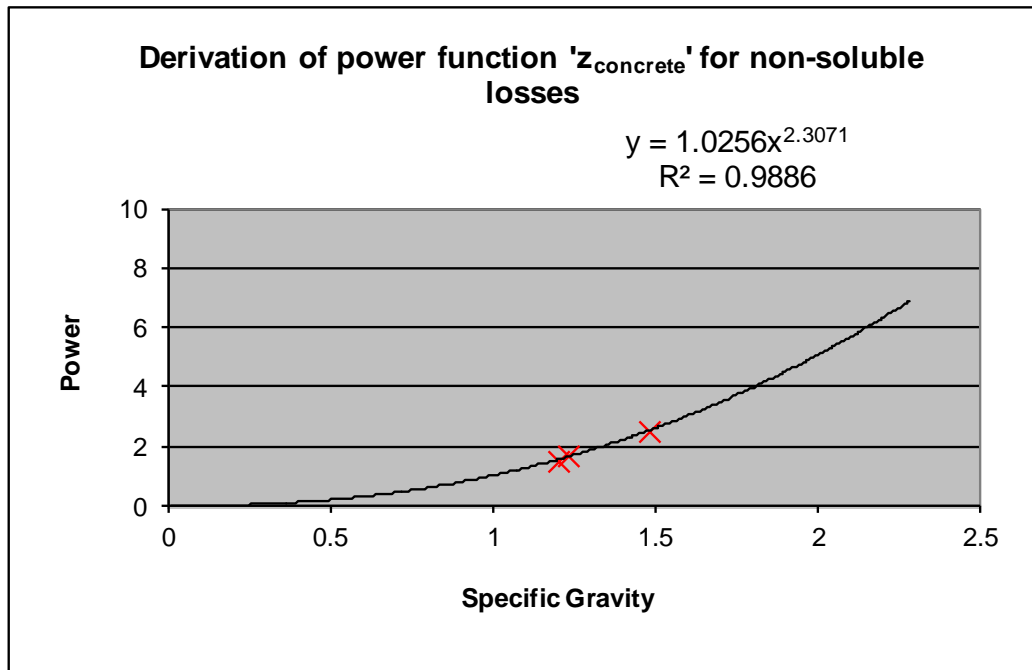


Figure A3.1-8 Derived relationship between specific gravity and the non-soluble loss power reduction value $z_{concrete}$ for wash-off volume-steps.

The form of this equation means that the higher the compound specific gravity, the greater the power value and thus the smaller the fraction derived using equation 20. In other words, for equivalent wash-off steps, the higher the compound specific gravity, the smaller the fraction of non-soluble phase losses.

Derivation of the power function $z_{asphalt}$ was not possible using the measured data as the amounts of non-soluble losses on this type of surface are too small to give a robust estimation of any reductions over successive wash-off steps. Instead an equation for calculating $z_{asphalt}$ was derived on a theoretical basis assuming that the function takes the same form as equation 22 but the power value for reduction of non-soluble losses is greater on asphalt than on concrete. This assumption is based on the probability that it is more difficult to move non-soluble material over the asphalt surface than the concrete surface, especially after most of the more easily moved compound has been lost

in the first wash-off step. The derived relationship is shown in Figure A3.1-10 and enables a value for $z_{asphalt}$ to be derived as follows:

Equation 24

$$z_{asphalt} = 1.1387 \times \text{Specific Gravity}^{2.3879}$$

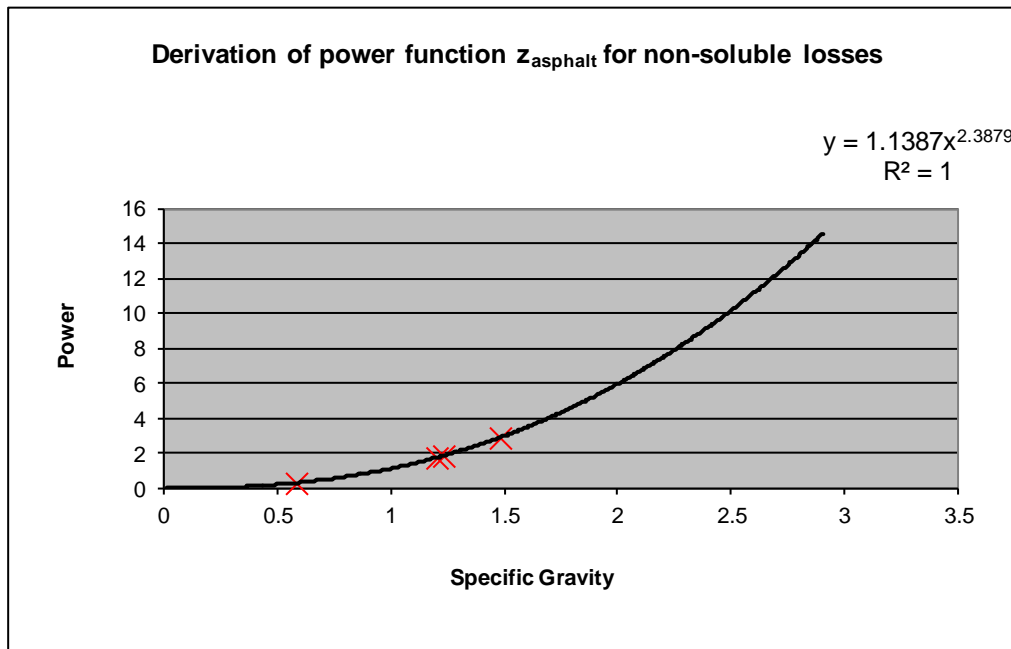


Figure A3.1-9 Derived relationship between specific gravity and the non-soluble loss power reduction value $z_{asphalt}$ for wash-off volume-steps.

Step 4

Successive 0.5 mm rainfall wash-off steps continue until the daily rainfall event is completed. At this stage, some of the mass remaining is sorbed to the surface and some may remain on the surface in non-soluble form. The remaining compound in both phases then degrades over the period of volume until the next rainfall event. The mass remaining after degradation is calculated as follows:

Equation 25

$$\text{Mass remaining} = M_1 \times \text{EXP}(-(d \times \text{LN}(2)) / \text{DT50}_{\text{hard surface}})$$

Where M_1 is the mass remaining at the end of the rainfall event.

d is the number of days between rainfall events.

$DT50_{hard\ surface}$ is the half life for a specific surface type.

There are no differences in $DT50_{hard\ surface}$ values used to calculate degradation in either the sorbed or non-sorbed phases.

Step 5

For the succeeding rainfall events, the wash-off processes are repeated except that:

- 5a.** The initial amounts of sorbed and non-sorbed (if relevant) compound in the first wash-off step of the subsequent events are calculated from the total mass remaining at the start of the time step (following degradation during the time between rainfall events), and distributed according to the ratio of sorbed and non-sorbed compound at the end of the previous rainfall event.
- 5b.** The time steps for wash-off are not re-set to $n = 1$ at the start of successive rainfall events but instead are re-set to $n =$ the number of the rainfall event following application. Thus the first wash-off step at the start of the second rainfall event after application is re-set to $n = 2$, and so on. This is because it is assumed that, following the first rainfall event after application, compound remaining on the surface becomes increasingly 'stabilized' so that subsequent rainfall events become increasingly less effective at washing it off.
- 5c.** Because of this 'stabilizing' effect, the time steps for calculating the de-sorption volume fraction and the non-soluble mass lost are not re-set at the start of successive rainfall events but continue increasing throughout the simulation period.
- 5d.** On concrete, it is assumed that during the time between the end of the first rainfall event and the start of the second, the 'stabilization' process results in all the compound remaining on the surface becoming effectively 'sorbed' so that subsequent wash-off losses are determined only by de-sorption processes. This is not the case on asphalt, where significant amounts of non-sorbed material remain 'trapped' in surface crevices and are only subject to the usual processes of solute formation by a decreasing fraction of run-off water moving over the surface.

A3.2 THE BALLAST LEACHING SUB-MODELS

The Ballast leaching sub-model calculates the mass of herbicide leached out of a ballast column with a surface area of 0.492 m² and a depth of 0.6 m. The volume of the column is thus 0.2952 m³, and the ballast within it has a mass of 600 kg. The model incorporates the following steps:

Step 1

Following application, herbicide compound is present only at the surface or the upper few mm of the ballast column. At this stage no sorption is specified in the model.

Step 2

During the first drainage step of the model, which is equivalent to the first 0.25 L of leaching per 0.492 m² of surface, rainfall impacts on the surface, interacts with the compound, and forms solute. Increasing amounts of rainfall start to wet up the ballast column but no drainage occurs until the capacity of the column to retain water is reached. At this stage, depending on the solubility of the compound, some of the applied mass remains on the surface in non-soluble form and some has formed solute in the water retained in the column. The mass in solution partitions to the fine material within the column, which comprises both mineral and organic components, and an equilibrium is established between the sorbed and non-sorbed phases. Further rainfall during this step initiates the first 0.25 litres of drainage out of the ballast column. The mass of soluble herbicide leached out of the ballast column in this 'mobile' drainage volume represents the interaction between the additional rainfall, the pool of non-soluble material remaining at the surface and the amount of solute in the retained water fraction following the initial partitioning.

2a Calculation of the initial mass of compound in the water retained in the column and available for partitioning.

The mass of herbicide in solution in the retained water of the ballast column before partitioning occurs is calculated from the solubility of the compound (mg L⁻¹) and the volume of retained water in the ballast column. This volume is derived from measurements taken during the controlled wash-off study (Shepherd & Heather, 1999) and, for the 0.2952 m³ ballast column used in this sub-model is equivalent to 0.6 litres. For compounds with very high solubility, the mass that goes into solution is limited by the total mass of compound at the ballast surface at the start of the rainfall event.

Equation 1

*Mass in solution (M_{sol-i}) = EITHER: $[(0.6 \times \text{compound solubility (mg L}^{-1}\text{)}]$, OR:
(Initial mass at the ballast surface, M_i). Whichever is the smaller value.*

If compound solubility is so large that all of the mass reaching the surface of the ballast column goes into solution in the retained water fraction, then no non-soluble material remains on the surface. For less soluble compounds, a pool of non-soluble material remains at the surface, the amount being the difference between the calculated mass impacting on the surface and the mass that goes into solution in the retained water fraction.

Equation 2

Non-soluble mass remaining after initial solute formation (N_r) = $M_i - M_{sol-i}$

2b Calculation of the initial mass sorbed to ballast organic matter.

Partitioning between the aqueous and sorbed phases in the ballast column is calculated from the compound Koc, the volume of retained water in the column and the total mass of organic carbon in the column, as specified in the Groundwater Scenario characteristics (see section 3.2.2 of the main report). Partitioning is assumed to be instantaneous;

Equation 3

Mass sorbed (M_{sorb-i}) = $M_{sol-i} \times \{1 - (0.6 / [(0.6 + (O_m \times Koc)])\}$

Where O_m = Mass of organic carbon in the ballast column.

The mass remaining in solution after sorption is then calculated as:

Equation 4

Mass in solution after sorption (M_{sol-p}) = $M_{sol-i} - M_{sorb-i}$

2c Calculation of the mass of compound washing through the column in the mobile water.

Further rainfall during the step initiates the first 0.25 litres of drainage out of the ballast column. If a non-soluble pool of compound remains at the surface, then this further rainfall interacts with the compound, forms additional solute and moves through the ballast column as a mobile solute component. The amount of compound washed into the ballast column during this stage is determined by the surface area of interaction between the non-soluble pool at the surface and the amount of incident rain forming mobile phase water (0.25 litres in this volume step). It is thus a surface-specific fraction of the non-soluble material remaining at the surface, although the amount is limited by the compound solubility and the volume of mobile phase water (0.25 L). Derivation of the fraction of the non-soluble pool washed into the ballast column was by calibration and the derived value is 0.024. This value gave the best overall fit to the mean measured masses of atrazine, diuron, oryzalin, isoxaben and oxadiazon lost in the first 0.25 litres

of leachate collected from ballast columns during the controlled wash-off study (Shepherd & Heather, 1999). The mass of compound in the mobile water phase is thus calculated from:

Equation 5

$$\begin{aligned} \text{Mass in ballast mobile water fraction } (M_{sol-mob}) &= \\ \text{EITHER: } (N_r) \times 0.024 & \\ \text{OR } 0.25 \times \text{compound solubility (mg L}^{-1}\text{).} & \text{ Whichever is the smaller value.} \end{aligned}$$

If there is no non-soluble pool of compound left at the surface of the ballast column following solute formation in the retained water fraction, then $M_{sol-mob}$ is zero.

The calculated mass of compound in the mobile water fraction is then used to calculate the mass of non-soluble compound remaining at the surface at the end of the first drainage step:

Equation 6

$$\text{Non-soluble mass remaining at end of volume step } (N_1) = N_r - M_{sol-mob}$$

2d Calculation of the mass of compound sorbed from the mobile water phase.

As it moves through the ballast column, the mobile solute component also partitions to the organic matter within the ballast, although only a small fraction of the organic component participates because most of the mobile solute effectively by-passes it. The fraction of organic carbon mass in the ballast column that participates in mobile water phase sorption is also a surface-specific characteristic and is thus the same value (0.024) as that calibrated for the fraction of non-soluble compound at the surface that goes into solution in the mobile water volume. The mass of compound sorbed from the mobile water phase is calculated as:

Equation 7

$$\begin{aligned} \text{Mass sorbed from mobile phase } (M_{sorb-mob}) & \\ = M_{sol-mob} \times \{1 - (0.25 / [(0.25 + (O_m \times 0.024 * K_{oc}))])\} & \end{aligned}$$

2e Calculation of the mass of compound lost in the first 0.25 litres of leachate.

The mass of compound remaining in the mobile water phase following sorption is lost directly as leachate from the column. This mass is calculated from:

Equation 8

$$\text{Mass lost directly from the mobile water phase } (M_{leach-mob}) = M_{sol-mob} - M_{sorb-mob}$$

However, as the mobile phase water moves through the ballast column, it also interacts with and displaces a fraction of the solute mass in the retained water and removes it in the leachate. This

fraction represents the zone of interaction between the mobile and retained water fractions in the ballast column and its value of 0.051 has been calibrated using the mean measured mass of an un-named compound lost in the first 0.25 litres of leachate collected from ballast columns during a confidential ballast leaching study. This compound is so soluble that all the applied mass goes into solution in the retained water phase during the first volume step and thus the measured losses relate solely to the mass displaced from retained water component of the ballast column. It also has a very low sorption so that any uncertainties related to the extent of sorption within the ballast column are minimised. Nevertheless, sorption within the ballast column needs to be taken into account and the calculation for deriving the fraction of compound mass displaced from the ballast retained water was thus calculated from:

$$\frac{\text{Measured mass of compound lost in the first 250 ml of ballast leachate}}{(\text{Mass of compound applied} - \text{mass sorbed in the ballast column})}$$

A value of 0.051 was obtained and the mass of compound displaced from the retained water phase and lost in the first 0.25 litres of leachate is thus calculated from:

Equation 9

$$\text{Mass lost from the retained water phase } (M_{\text{leach-ret}}) = M_{\text{sol-p}} \times 0.051$$

The total mass of compound lost in the first 0.25 litres of leachate from the ballast column is thus:

Equation 10

$$\text{Total mass lost in the first 0.25 L of leachate } (M_{\text{leach}}) = (M_{\text{leach-mob}} + M_{\text{leach-ret}})$$

2f Calculation of the mass of compound remaining in the sorbed and solute phases of the retained water at the end of the drainage step.

At the end of the drainage step, the mass of compound remaining in the sorbed and solute phases of the retained water component of the ballast column are calculated as follows:

Equation 11

Total mass remaining in the sorbed phase of the column at the end of the drainage step

$$(M_{\text{sorb-f}}) = (M_{\text{sorb-mob}} + M_{\text{sorb-i}})$$

Equation 12

Total mass remaining in the solute phase of the column at the end of the drainage step

$$(M_{\text{sol-f}}) = (M_{\text{sol-p}} - M_{\text{leach-ret}})$$

Step 3

At the start of each subsequent drainage step, each of which is equivalent to 0.25 litres of leachate per 0.492 m² area of railway ballast, the sorbed mass and remaining solute mass in the retained water component of the ballast column re-equilibrate. Incident rainfall continues to wash fractions of the non-soluble compound remaining at the surface into the ballast column in the mobile water fraction and, as this moves through the column, it continues to interact with solute in the retained water fraction. The resulting soluble mass in the mobile water is then removed out of the column in each 0.25 litres of leachate.

3a Calculation of the mass of compound washing into the column in the mobile water.

If there is any non-soluble pool of compound remaining at the surface then, as with the first volume step, continuing rainfall interacts with it to form solute and moves through the ballast column as a mobile solute component. However, the fraction of the non-soluble mass remaining at the ballast surface that interacts to form solute increases slightly with each drainage step. This is because of the increasing force acting on the non-soluble pool at the surface as rainfall volume increases. The fraction increases according to a power function of the volume step number, the function being derived by calibration using results from the controlled wash-off study (Shepherd & Heather, 1999) and a subsequent wash-off study undertaken using atrazine and 15 mm of applied rainfall. The power function takes the form:

$$0.024 \text{ (Fraction used in the first volume step)} \times [n^{0.09}]$$

Where n is the number of the volume step.

For each subsequent drainage step in the sub-model therefore, the mass of compound washed into the ballast column with the mobile water fraction is calculated from:

Equation 13

Mass in ballast mobile water fraction ($M_{sol-mob}$) =

EITHER: $(N_r n) \times [0.024 \times (n^{0.09})]$

OR: $0.25 \times \text{compound solubility (mg L}^{-1}\text{)}$. Whichever is the smaller value.

Where n is the number of the drainage step.

3b Calculation of the mass of compound displaced from the retained water solute mass.

In contrast to the step-dependent increase in the fraction of non-soluble mass forming solute in the mobile water phase, the fraction of solute that is displaced from the retained water phase by the mobile solute component moving through the ballast column decreases with each successive drainage-step as the mass in the retained water fraction becomes increasingly depleted and less subject to interaction with the mobile water. This decrease takes an exponential form and has been calibrated using results from the same controlled wash-off study used to derive the mass

displaced from the retained water in the ballast column during the first volume step. This compound was used because it is so soluble that all the applied mass goes into solution in the retained water phase during the first drainage step and thus all subsequent losses result from displacement of mass from the retained water phase in the ballast column. The exponential relationship takes the form:

$$0.051 \text{ (Fraction used in the first drainage step)} \times [\text{EXP} (-0.037 \times n)]$$

Where n is the number of the drainage step.

Using this relationship for the un-named compound, together with the calculated masses sorbed within the ballast column per drainage step, gives a very good fit to the measured accumulated mass lost as can be seen from Figure 3.1.2-6 in the main report. The relationship between the measured and predicted accumulated mass values has an r^2 value of 0.9958.

For each subsequent drainage step in the sub-model therefore, the mass of compound lost in the leachate via displacement from the ballast column retained water fraction is calculated from:

Equation 14

$$\text{Mass lost from the retained water phase } (M_{\text{leach-ret}n}) = M_{\text{sol-p}n} \times 0.051 \times [\text{EXP} (-0.037 \times n)]$$

All other leachate mass calculations are the same as those used for the first drainage step.

Step 4

Successive 0.5 mm rainfall drainage steps continue until the daily rainfall event is completed. At this time, some of the mass remains in solute form in the retained water component of the ballast column, some remains sorbed to the ballast organic carbon component and some may remain on the surface in non-soluble form. During the time between each daily rainfall event, the entire remaining compound degrades as determined by the time between rainfall events and the surface-specific degradation rate. The different masses remaining after degradation are calculated as follows:

Equation 15

$$\text{Mass remaining} = M_1 \times \text{EXP}(-(d \times \text{LN}(2)) / \text{DT50}_{\text{ballast}})$$

Where M_1 is the mass remaining at the end of the rainfall event.

d is the number of days between rainfall events.

$\text{DT50}_{\text{ballast}}$ is the half life for used ballast.

There are no differences in the $DT50_{\text{ballast}}$ values used to calculate degradation in either the sorbed or non-sorbed phases within the ballast column or in the non-soluble pool remaining at the surface.