

Herbicide partitioning to concrete, asphalt and railway ballast

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FOREWORD

This report presents the results of a laboratory study quantifying the concrete and asphalt partition coefficients for several herbicides. The findings are discussed in the context of herbicide dynamics in urban areas.

Reference to this report should be made as follows:

Ramwell CT (2002). Herbicide partitioning to concrete, asphalt and granite ballast. Cranfield Centre for EcoChemistry research report No. JA3753e for PSD, 30 pp.

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

EXECUTIVE SUMMARY

Following herbicide application to hard surfaces (concrete, asphalt and railway ballast) only a proportion of the applied active substance is detected in runoff, and the fraction unaccounted for differs between compounds and surface types. Attempts to predict herbicide losses in the urban environment have been hindered by the fact that it is not known to what extent, if any, sorption can account for the retention of herbicides to the surface.

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. A partition coefficient was determined after 144 hours.

The partition coefficients for fluoranthene, phenanthrene, atrazine, diuron, oryzalin, isoxaben, isoproturon and dichlorophen on asphalt and concrete were determined. There was significant partitioning of compounds to asphalt and an exponential relationship with literature-values of K_{oc} existed. The relationship between K_p for concrete and literature-values of K_{oc} was weaker. Furthermore, there was no significant sorption of herbicides to granite ballast. It is probable that physical processes are also important to describing herbicide losses from hard surfaces.

The measured partition coefficients can be used to improve the ability of a basic risk assessment model to predict the environmental concentration of different compounds applied to hard surfaces.

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1. INTRODUCTION

Regulation of herbicides used on land not intended to bear vegetation is restricted by the lack of knowledge on their fate and behaviour following application. Treated areas commonly include pavements, roadsides and railways. These areas are designed to be impermeable and facilitate the rapid drainage of runoff. Consequently, the potential for herbicide retention and subsequent degradation is minimised, whereas the potential for the removal of herbicides and subsequent entry into surface waters is augmented.

Previous studies have demonstrated that following herbicide application only a proportion of the applied active substance may be detected in runoff, the remaining being unaccounted for, and the percentage loss of herbicides differs between compounds and surface type (Ramwell *et al.*, 2002; Shepherd & Heather, 1999). These studies have been used to develop a Tier 1 model to enable the prediction of surface water exposure based on knowledge of the application rate, the soil organic carbon partition coefficient (K_{oc}) and the solubility of the compound applied (Hollis *et al.*, 2000). However, the use of this model for regulatory purposes is restricted to five compounds, and it is limited by the tenuous link between K_{oc} and partitioning to the hard surface. In soils, herbicide sorption is largely driven by the organic carbon content (Nicholls, 1991), thus K_{oc} is fundamental to leaching models, hence its use in the Tier 1 model. However, soils and hard surface materials are intrinsically different, and the validity of the extrapolation used for the Tier-1 model is unknown.

In the soil, pesticides are in contact with a 3-dimensional 'volume' of soil, whereas on hard surfaces pesticides remain in contact with only a 2-dimensional 'area' of material. Consequently, existing tests for the adsorption/desorption of pesticides to soil may not be suitable for representing processes occurring on hard surfaces. To date, there are no means by which to quantify adsorption/desorption processes to hard surface materials, nor is the extent to which this process influences herbicide loss known.

In order to give more confidence in the model, and to enable extension of the model to other compounds, factors affecting the partitioning of substances to hard surfaces need to be established. To achieve this, initially, there needs to be an experimental procedure in place for determining partition coefficients ($K_{p,s}$) for the main hard surface types (asphalt, concrete, railway ballast). Partition coefficients for compounds with a range of physico-chemical characteristics can then be determined. The results could also reveal processes other than sorption that may be influential factors in determining the fate of herbicides applied to hard surfaces, and the relative importance of different processes could depend on the properties of the compound. The measured partition coefficients can

be used to establish whether there is a relationship with existing physico-chemical properties such as K_{oc} to enable predictions of K_p for non-tested compounds. It should be noted that there has been no attempt to identify detailed adsorption or absorption processes whether physical and/or chemical. Throughout this report the term partitioning and sorption are used synonymously to describe the adherence of a herbicide to a surface as measured by the difference in concentration of the solution between different time points.

The aim of this study was to investigate the behaviour of herbicides exposed to hard surface materials. The objectives of the research were to develop a method for determining a partition coefficient for hard surfaces, determine the K_p for a range of compounds and to examine factors affecting the replicability of the test.

2. MATERIALS AND METHODS

The principle of the experimental procedure outlined by the OECD (1998) for chemical sorption and desorption from soil monitoring the change in concentration of a herbicide solution when in contact with three different soil types was adopted for this study. In the current study surfaces of a test material (concrete, asphalt or granite ballast) were exposed to a herbicide solution of known concentration and aliquots of this solution were taken at fixed time periods to assess any change.

Emphasis was placed on establishing the partition coefficient for a number of compounds to increase the confidence of any subsequent relationship with literature values of K_{oc} . Quantification of herbicide loss following spray application at the laboratory scale was secondary, and was thus performed on fewer compounds than the sorption studies.

2.1 Hard surface materials

Granite ballast used by the railway industry (graded to 500 mm) was obtained from a local quarry. Small concrete slabs (0.10 m x 0.15 m) were created by cutting up commercially-available paving slabs that are normally used for pavements (as opposed to those used for landscaping domestic gardens). Asphalt slabs were made using 30/14 wearing course asphalt (BS954 T6C6/4 50P H). This asphalt is primarily used as the surface layer on main roads. Hot asphalt was poured into wooden frames (0.15 m x 0.4 m) and compacted using a vibrating roller. This was left for 24 hours to solidify after which the resulting slabs were cut to form 0.10 m x 0.15 m slabs. All surfaces were washed with tap water and left to air dry prior to use.

2.2 Method development

Initially, a non-herbicidal organic compound with a high K_{ow} was used to determine whether there would be any measurable partitioning to asphalt, concrete and granite ballast, and to assess the suitability of the experimental design in terms of losses to the apparatus. This work is described in detail in Appendix 1. The results were used to define the experimental procedure for the main study.

2.3 Sorption study

For concrete and asphalt, the test solution was contained in Pyrex dishes using glass beads to raise the slabs at each corner (Figure 1). The volume of solution used (250 ml) was such that, when in position,

approximately 3 mm depth of the slab was exposed to the solution ensuring that the wearing course was the main sorption site.



Figure 1 Experimental apparatus for the sorption study

Prior to being placed in the herbicide solution, the test surface was placed in distilled water (250 ml) for 16 hours, after which it was removed and left to dry for 1 hour to standardise the moisture content of each replicate. Herbicide solutions were prepared in a 10-L aspirator to ensure an even distribution of the compound when decanted into separate dishes. Distilled water was used as the solvent. The required concentration was calculated by dividing the mass of active that equated to label-application rate of a 0.015 m² area, by the nominal volume of 250 ml. If this concentration was greater than the solubility limit, a concentration slightly lower than the solubility limit was used. The concentrations used are detailed in Appendix 2. Magnetic stirrers were used to agitate the solution.

For ballast, 0.5 kg of the stones was placed in a stainless steel container and the herbicide solution was poured over the entirety of the ballast. The containers were stacked and a shaker (Vibramax 100, speed 2) was used to agitate the solution. Herbicide solution held in the Pyrex dishes and stainless steel containers with no hard surface served as a control. In addition, concrete and asphalt slabs were placed in distilled water to ensure no leachates were present that could interfere with analysis. A fourth control was included for some experiments where 3 mg of Ca(OH)₂ was added to the herbicide solution. This control was to assess the influence of calcium leaching from concrete surfaces.

Samples (1ml) were taken from all containers prior to slabs being placed in the herbicide solution (T_0) and after 2, 6, 24, 72 and 144 hours (T_2 , T_6 , T_{24} , T_{72} and T_{144} respectively).

At the end of the experimental period (144 hours) the slabs were removed from the herbicide solution and left to air dry for 24 hours. After drying, the slabs were rinsed in distilled water (250 ml) for 10 seconds after which they were placed on glass beads in a separate 250 ml of distilled water. Samples were taken from the rinse water and from that contained in the vessel after 1 and 24 hours. After 24 hours the water was replaced with fresh distilled water (250 ml) and samples taken after 144 hours. The solution was agitated prior to sampling.

All samples were stored in glass vials at 4°C prior to analysis. The study was conducted at 18°C in the dark and all tests were performed in triplicate. The above method formed the basis for the sorption experiments for all compounds investigated. The only deviations from the above described method were for isoxaben, oryzalin and dichlorophen where the aliquot sample was 0.7 ml to which 0.7 ml of HPLC-grade methanol was added, and for oxadiazon where 0.5 ml of HPLC-grade methanol was added to 0.5 ml of the aliquot and these samples were stored at -18°C.

2.4 Desorption Study

The desorption study was designed to quantify losses following application by spraying. The concentrations of the herbicide solutions were such that a millilitre of solution contained the mass of active that equated to label-application rate for a 0.015 m² area. An air propellant device adopted to fit a 1.8 ml glass vial was used to spray the herbicide solution (1 ml) onto the hard surfaces. For herbicide products, distilled water was used as the carrier, but for the technical grade, methanol was used. The spray lines were rinsed three times with 0.25 ml of solvent and the rinsings sprayed onto the slab. Two methanol-washed filter papers (Whatman 42, 24 cm Ø) were placed underneath the slabs during spraying to intercept any drift or drips that may have occurred during application. Control sets were made by spraying the hard surface as above using the solvent alone. The hard surfaces were left to dry for 24 hours after which they were rinsed for 10 seconds in distilled water (250 ml) before being transferred to clean distilled water (250 ml), the apparatus being as illustrated in Figure 1. Samples were taken from the rinse water and then after 1 and 24 hours. After this time, the slab was removed into a different dish containing a further 250 ml of distilled water. Samples were then taken after 48, 72 and 144 hours since the first rinse. The pH of the solution was taken at the end of each experiment. All samples were stored in glass vials at 4°C prior to analysis. The study was conducted at 18°C in the dark and all tests were performed in triplicate.

A full millilitre of herbicide solution was sprayed directly onto two filter papers, followed by the rinsings from the spraying apparatus. Following rinsing, three 0.25 ml volumes of solvent were sprayed onto another filter paper. All the filter papers were cut into pieces (*c.* 2 cm²) and placed into glass bottles. Methanol (100 ml) was added to extract any herbicide. These were stored at 4°C prior to analysis.

2.5 Experimental investigations

2.5.1 Compounds

Atrazine, diuron, oxadiazon, oryzalin and isoxaben were used in the development of the Tier 1 risk assessment model for use in urban environments, thus it was necessary to establish partition coefficients for these compounds to enable any amendments to the model to be made, and these compounds were considered as 'standard'.

To extend the range of physico-chemical properties represented additional compounds were investigated (phenanthrene, isotroturon and dichlorophen).

The technical grade compounds were used to remove any unknown variables associated with the formulated product. However, for a limited number of compounds the experiments were repeated with the formulated product to observe any differences with the technical grade.

2.5.2 Concentration effect

It was possible that the concentration of the herbicide solution could affect the degree of partitioning. A test was therefore conducted using a range of initial concentrations for a single compound (diuron).

2.5.3 Temperature effect

The surface temperatures of asphalt and concrete during the summer daytime can range from 20-40 °C (van Buren *et al.*, 2000; Kjelgren & Montague, 1998; Eliasson, 1996; Asaeda *et al.*, 1996). Thirty degrees centigrade was chosen as a representative high temperature and a small experiment, detailed in Appendix 3, was undertaken to establish the conditions necessary to achieve this (30 minutes in the oven at 50 °C). For many herbicides, it is advised that application does not occur below an air temperature of 5°C, thus for a representative low temperature the test surfaces were placed in a refrigerator giving a surface temperature of 13°C. Concrete and asphalt stored at room temperature had a surface temperature of 18°C. In addition, a parallel study was performed where the entire experimental apparatus were stored at 5°C.

2.5.4 Moisture effect

It is possible that herbicide is physically translocated to within the concrete or asphalt matrices. The initial moisture content of the test surface may therefore influence sorption. To test this theory, comparisons of dry surfaces, moist and visibly wet surfaces were made. Slabs were moistened by soaking them in water (250 ml) for 16 hours and leaving them to air-dry for one hour and dry slabs were not exposed to any water. Wet slabs were soaked for 16 hours in water (250 ml) and, after allowing excess surface-water to drain for one minute, the slabs were placed in herbicide solution. Tests demonstrated that surfaces exposed to water for longer (120 h) did not gain significantly more weight than those exposed to water for only 16 hours. The moist slabs were visibly dry after the one hour air drying; however the weight of the slabs was still higher than the initial weight.

2.6 Ratio of cement

To assess whether the composition of the concrete affected sorption, concrete containing different proportions of cement were compared. Concrete was made by mixing 1 part cement (Mastercrete Portland Cement) to either 3 or 6 parts of a shingle and sand aggregate. Concrete was poured into paper-lined, wooden moulds (0.4 m x 0.15 m) and levelled. When dried, the resulting slabs were quartered to give the standard size of test surface (0.10 m x 0.15 m). The hand-made concrete surfaces were compared to the pre-cast, commercially available concrete as used throughout the rest of the study.

2.7 pH

A detailed investigation into the change in pH of distilled water in the presence of the hard surfaces was undertaken. In addition, the pH of the herbicide solution was taken at the beginning and end of the experiment.

A summary of the different tests undertaken and the compounds used is given in Appendix 4.

2.8 Chemical analysis

The analysis of all the compounds was performed on a Summit HPLC system consisting of a P580 gradient pump, GINA50 autosampler with integral rheodyne injection valve and UVD170S UV-VIS detector (Dionex). The system was fully automated using Chromeleon software. Separations were performed on a GENESIS 4- μ m C18 reversed phase column (150mm x 4.6mm internal diameter) (Jones Chromatography). The mobile phase was mixed and de-gassed on-line. The mobile phase, the eluent flow and the retention time differed between compounds; the details are summarised in Table

1. Calibration was performed using external standards. A quality control standard was analysed at the beginning and end of each technical run and after not more than every 15 samples.

	Mobile phase (%)			Flow rate (ml min ⁻¹)	Retention time (min)	UV Detection λ (nm)
	Methanol	0.05% TFA	Water			
Fluoranthene	90	-	10	1.5	4.0 ± 0.1	fluorescence
Phenanthrene	85	-	15	1.5	3.5 ± 0.1	fluorescence
Atrazine	65	-	35	1.0	3.7 ± 0.2	220
Diuron	65	-	35	1.0	6 – 8	220
Oryzalin	80	20	-	1.0	4.5 ± 0.1	239
Isoxaben	70	30	-	1.0	6.6 ± 0.2	254
Dichlorophen	75	25	-	1.0	7.1 ± 0.2	290
Isoproturon	50*	50	-	1.0	5.0 ± 0.1	250

*acetonitrile

Table 1 Summary of HPLC conditions

2.9 Data Analysis

The reported concentrations were converted to a mass to account for the change in volume of solution as samples were taken. In addition, to account for any changes in concentration that could occur in the absence of any hard surface (as indicated by the control sample) any partitioning to the hard surface was determined in relation to the mean concentration of the control at T_{144} . Partition coefficients were calculated as a ratio of the mass of herbicide partitioned to the hard surface area (mg m⁻²) after 144 hours (T_{144}) to the herbicide concentration of the solution after 144 hours. The mass of herbicide partitioned to the hard surface was calculated by determining the mean mass in solution of the control (no slab) and subtracting the mass in solution for each replicate exposed to a hard surface.

2.10 Comparison of measured K_p to K_{oc}

To assess whether there was a relationship between the measured K_p and existing physico-chemical properties of the compounds investigated, it was necessary to establish ‘literature’ values of such properties. A variety of sources was considered and these are detailed in Appendix 5. The fact that data from some of these sources may have had the same point of origin was taken into consideration.

3. RESULTS

Although oxadiazon was initially included in the experimental work, it transpired that the compound could not be analysed with the resources available. Given the range of compounds already examined, it was considered that the study would not be devalued by omitting this compound, thus no additional attempt was made to analyse any of the oxadiazon samples.

3.1 Partitioning to Granite ballast

Both fluoranthene and phenanthrene partitioned to granite ballast (Figure 2), but there was no significant partitioning of diuron or atrazine. Fluoranthene partitioning occurred within two hours, but there was no significant partitioning of phenanthrene to ballast until after six hours. Due to the paucity of any sorption of compounds with a high K_{ow} to granite ballast and the negligible sorption of atrazine and diuron, experiments using granite ballast were discontinued.

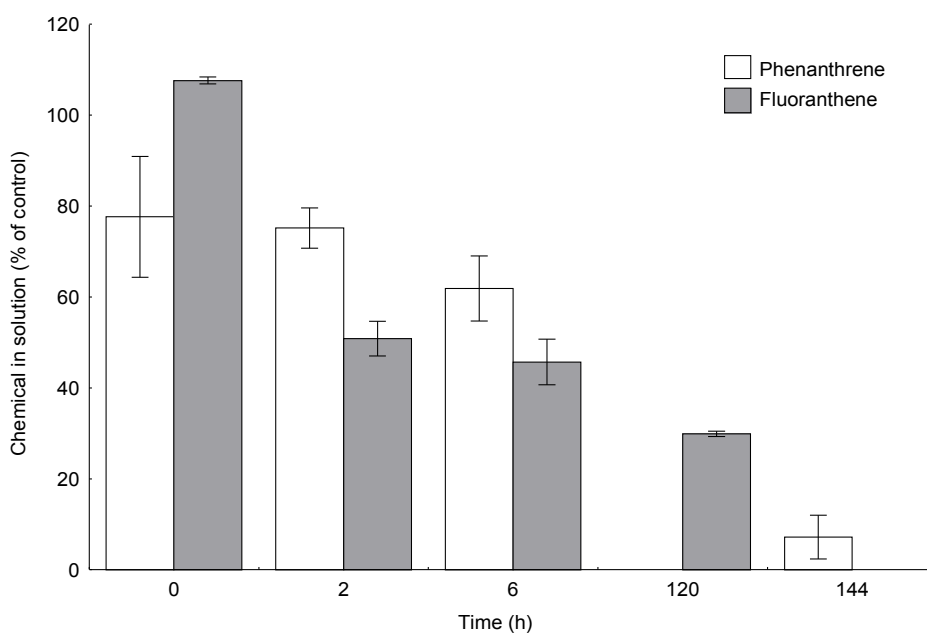


Figure 2 Decrease in fluoranthene and phenanthrene concentration in the presence of granite ballast

3.2 Partitioning to Asphalt

All compounds investigated partitioned to asphalt. For the compounds with a high K_{oc} (fluoranthene, phenanthrene and dichlorophen) there was significant partitioning to asphalt within hours (Figure 3). For the remaining compounds, there was little partitioning within 24 hours but significant differences between the compounds were noted after 144 h (Figure 4). Isoxaben sorbed most strongly for the low K_{oc} compounds with only 58% of the initial mass remaining in solution compared to 70% and 77% for oryzalin and diuron respectively. This compares to only 20% of dichlorophen remaining in solution after 144 hours.

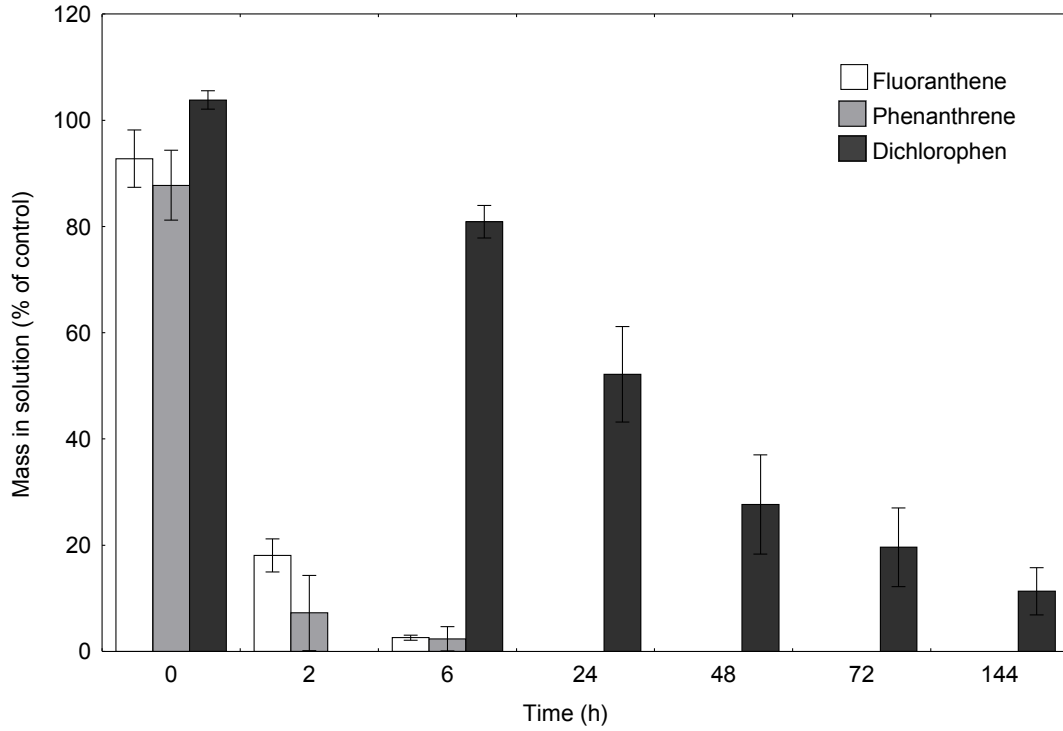


Figure 3 Decline in concentration of fluoranthene, phenanthrene and dichlorophen in the presence of asphalt showing the mean and ± 1 S.E.

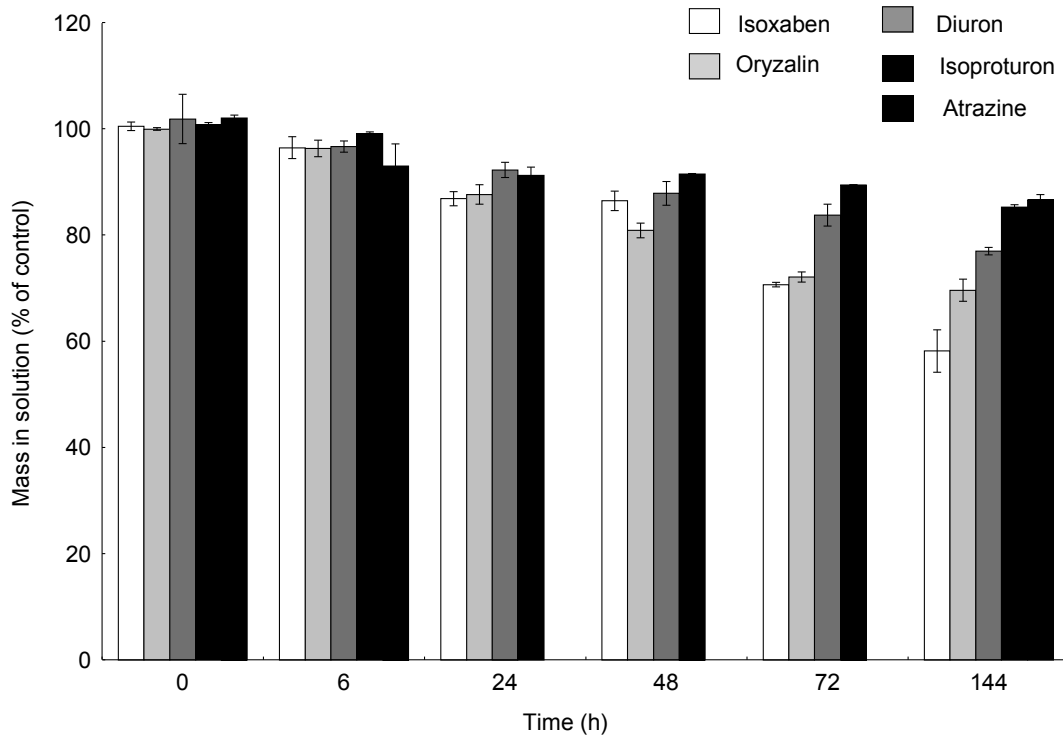


Figure 4 Decline in concentration of isoxaben, oryzalin, diuron, isoproturon and atrazine in the presence of asphalt showing the mean and ± 1 S.E.

3.3 Partitioning to Concrete

For all herbicides there was less partitioning to concrete than to asphalt with approximately 90% of the initial mass remaining in solution (Figure 5). Partitioning of fluoranthene and phenanthrene to concrete after 144 h was similar to the amount partitioned to asphalt after only two hours (*c.f.* Figure 3).

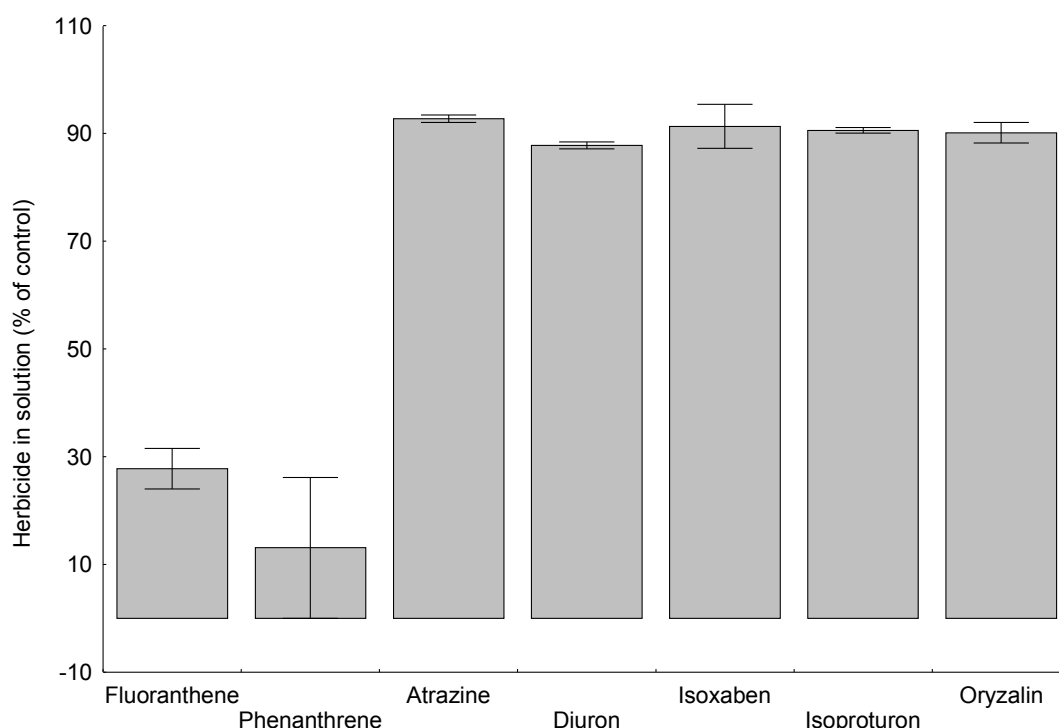


Figure 5 Herbicide remaining in solution when exposed to concrete after 144 hours showing the mean and ± 1 S.E.

3.4 Technical grade vs formulation

Sorption of the formulated product as well as the technical grade was investigated for atrazine, diuron and oryzalin. There were only minor differences in quantities sorbed after 144 h between the technical grade and the formulated product when in contact with asphalt and these differences were not consistent (Figure 6). For diuron, when considering the differences at T_0 , there was no significant difference in the quantities of a.i. sorbed when initially present as the technical grade or formulated product after 144 h. For atrazine, more partitioning occurred when the compound was present as the formulated product, but the converse was true for oryzalin. When exposed to concrete, there was no difference in the mass of atrazine sorbed when present as the technical grade or formulated product, and there was only a minor increase of diuron partitioning when present as the formulated product (Figure 7). For oryzalin there was an apparent increase in the mass of oryzalin in solution after 144 h when the formulated product was used.

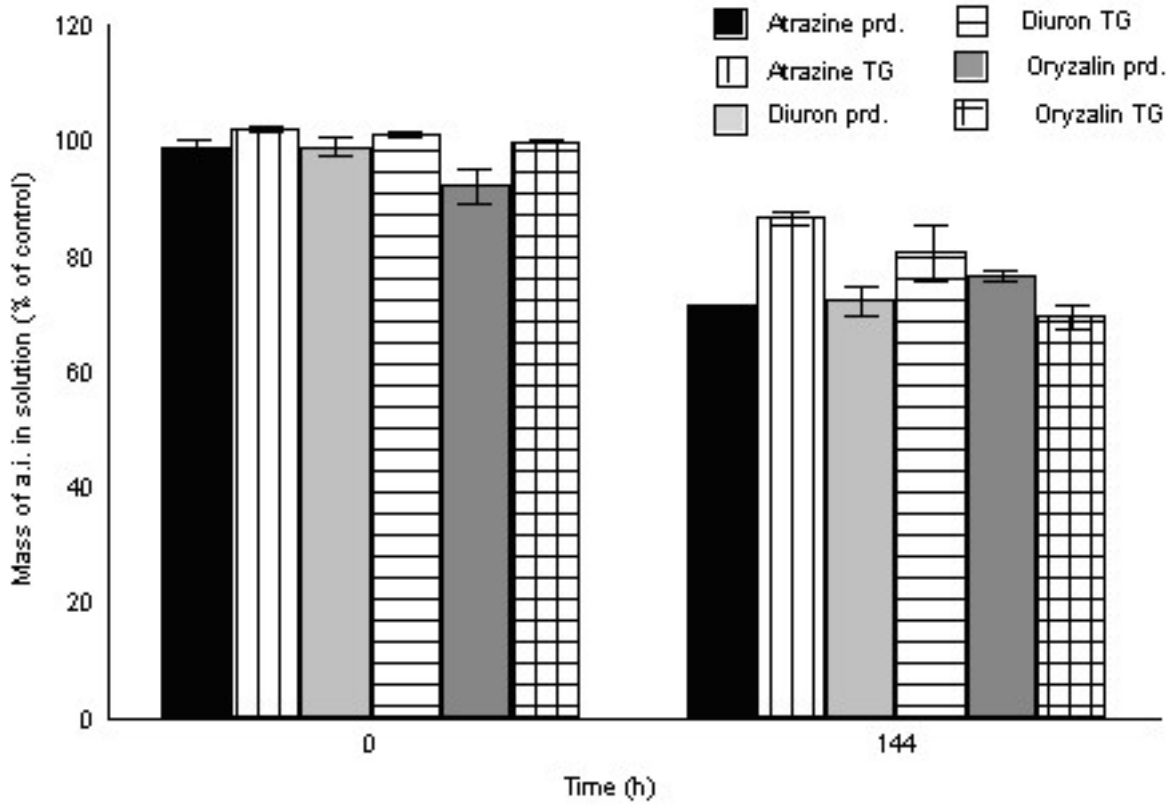


Figure 6 Comparison of a.i. remaining in solution after 144 h when present as the formulated product and the technical grade of atrazine, diuron and oryzalin in contact with asphalt

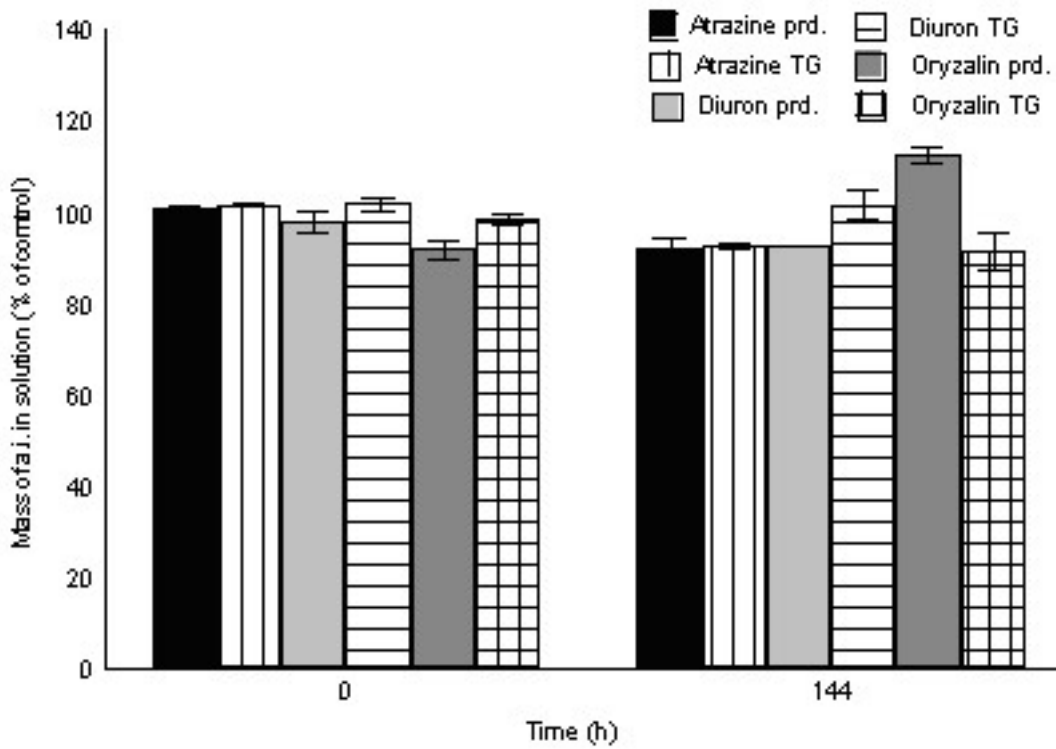


Figure 7 Comparison of a.i. remaining in solution after 144 h when present as the formulated product and the technical grade of atrazine, diuron and oryzalin in contact with concrete

3.5 pH

The pH of the solution changed in the presence of both concrete and asphalt. The pH of distilled water was 5.2 which increased to 8.9 for concrete and 6.0 for asphalt after 1 hour. After 144 hours the pH of water in the presence of concrete and asphalt was 8.7 and 7.7 respectively.

The addition of calcium carbonate to the herbicide solution to increase the pH of the solution had no significant effect on partitioning of neutral herbicides to concrete. However, samples analysed for dichlorophen recorded a higher reading when calcium carbonate was present compared to the control of no slab. For oryzalin, there was variability between the ‘no slab’ control and the calcium carbonate control but there was no overall difference.

3.6 Temperature effect

The initial temperature of the asphalt slab did not affect oryzalin partitioning. Partitioning to concrete was enhanced after 144 h when the slab had a surface temperature of 30°C, but the effect was minor (Figure 8). When the entire test was conducted at 5°C, there was no significant difference in partitioning of oryzalin to concrete compared to when the test was conducted at 18°C. The variability between concrete replicates was greater when the test was conducted at 5°C. Oryzalin partitioning at T_{144} to asphalt was approximately 7% greater when the test was conducted at room temperature than at 5°C.

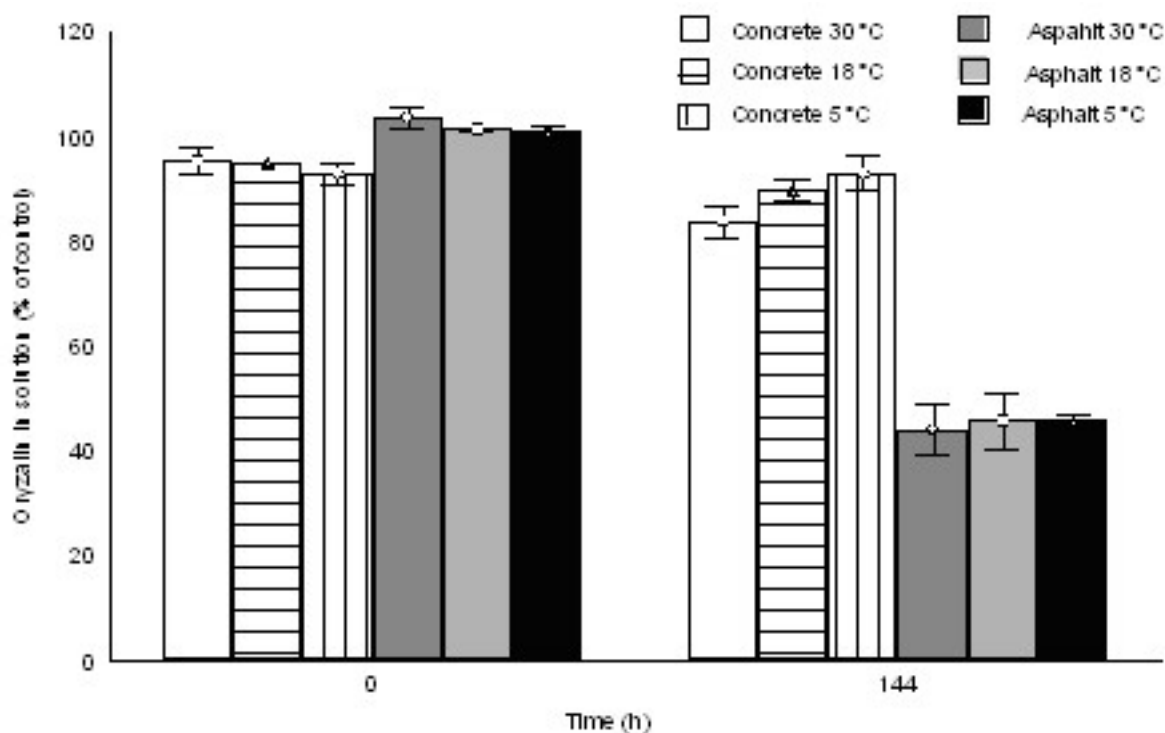


Figure 8 Comparison of a.i. remaining in solution after 144 h for different surface temperatures

3.7 Ratio of cement

There was no significant difference in the mean quantity of oryzalin partitioned to concrete comprising different cement ratios and commercially available concrete slabs. There difference in diuron sorption after 144 hours to the different concrete was marginal with 86% of diuron remaining in solution for concrete with a low cement ratio compared to 88% for a high cement ratio and commercially available concrete.

3.8 Concentration effect

The data were drawn from those experiments designed specifically to assess the effect of concentration and also from experiments containing control slabs under the different test conditions, for example investigating the effect of temperature and different cement compositions. There was no significant effect of the initial herbicide concentration on the partition coefficient after 144 hours, but there were a few anomalies (Figure 9).

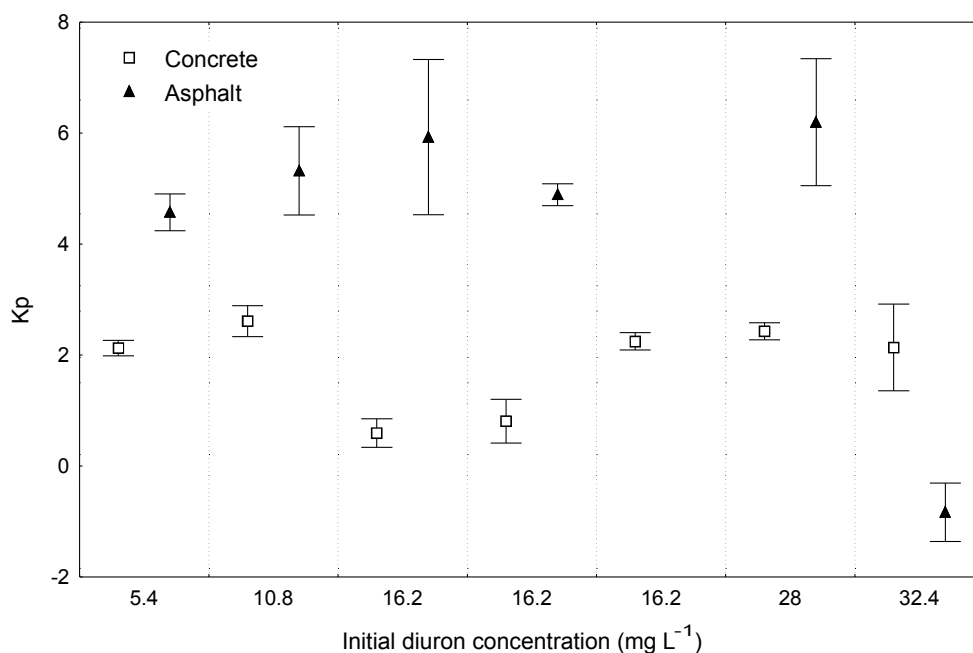


Figure 9 Comparison of diuron K_p between experiments

Diuron partitioning to concrete was *c.* 2 mg m⁻² but for two of the experiments the partition coefficient was *c.* 0.8. However, it was noted that for the studies with the lower K_p there was more interference in the chemical analysis (although this was consistent within the samples of individual experiments) than occurred for the other experiments. Although there was a general increase in the mean K_p for asphalt with increasing initial concentration, this was not significant due to the variability.

3.9 Partition Coefficients

The partition coefficients for each compound and test surface are given below detailing the range and mean of the replicates (Table 2). The coefficient of variation between the replicates tended to be larger for concrete than for asphalt.

	Asphalt K_p (mg m^{-2})				Concrete K_p (mg m^{-2})				Ballast K_p (mg kg^{-1})	
	Mean	Min	Max	CV%	Mean	Min	Max	CV%	Mean	CV%
Fluoranthene*	4600	3179	6375	35	44.7	30.1	52.4	28	0.28	12
Phenanthrene	774	-	-	-	16	-	-	-	0.29	0
Atrazine	2.53	2.20	2.95	15	1.28	1.09	1.54	18	0.007	108
Diuron	5.38	3.93	8.63	27	2.29	0.58	3.10	24	0	n/a
Dichlorophen	174	65.4	275	60	0.75	-0.2	2.38	188	n/a	n/a
Isoxaben	12.0	8.85	15.7	29	1.62	0.57	3.27	89	n/a	n/a
Isoproturon	2.83	2.55	3.32	15	1.70	1.43	2.24	27	n/a	n/a
Oryzalin	7.01	5.86	8.03	13	1.19	0.45	3.27	75	n/a	n/a

* K_p at T_{120}

Table 2 Partition coefficients for asphalt, concrete and granite ballast at T_{144}

Attempts to accurately measure a K_p for fluoranthene and phenanthrene were hindered by the rapid partitioning of these compounds to asphalt, and for fluoranthene the K_p was taken after 120 hours. For fluoranthene phenanthrene, the quantified K_p should be viewed as accurate to an order of magnitude due to difficulties in quantifying the low concentrations.

Comparison of the measured K_p to literature-values of K_{oc} indicated that there was a strong relationship between K_p with asphalt and K_{oc} , but a weaker relationship for concrete (Figure 10). The literature values varied depending on the source and a mean value was used (Appendix 4).

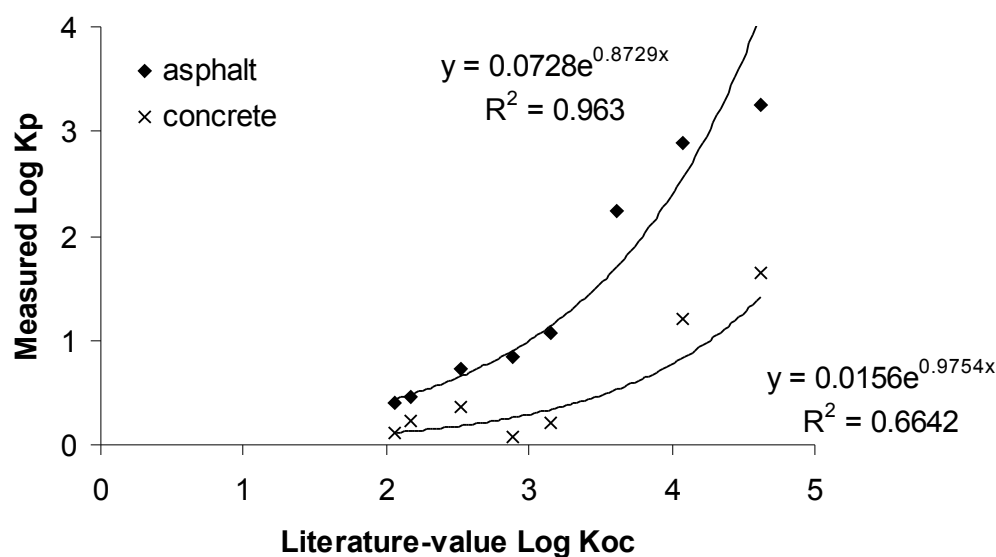


Figure 10 Relationship between literature-values of K_{oc} and measured values of K_p

3.10 Desorption from concrete and asphalt

The loss of technical grade atrazine and diuron following spray-application to concrete and asphalt was also investigated. There were measurable losses after rinsing the test surface for just 10 seconds in distilled water, during which time losses from concrete were higher than from asphalt (Figure 11). Over 50% of the total herbicide lost was removed within an hour, and for atrazine loss from concrete this proportion was 84%.

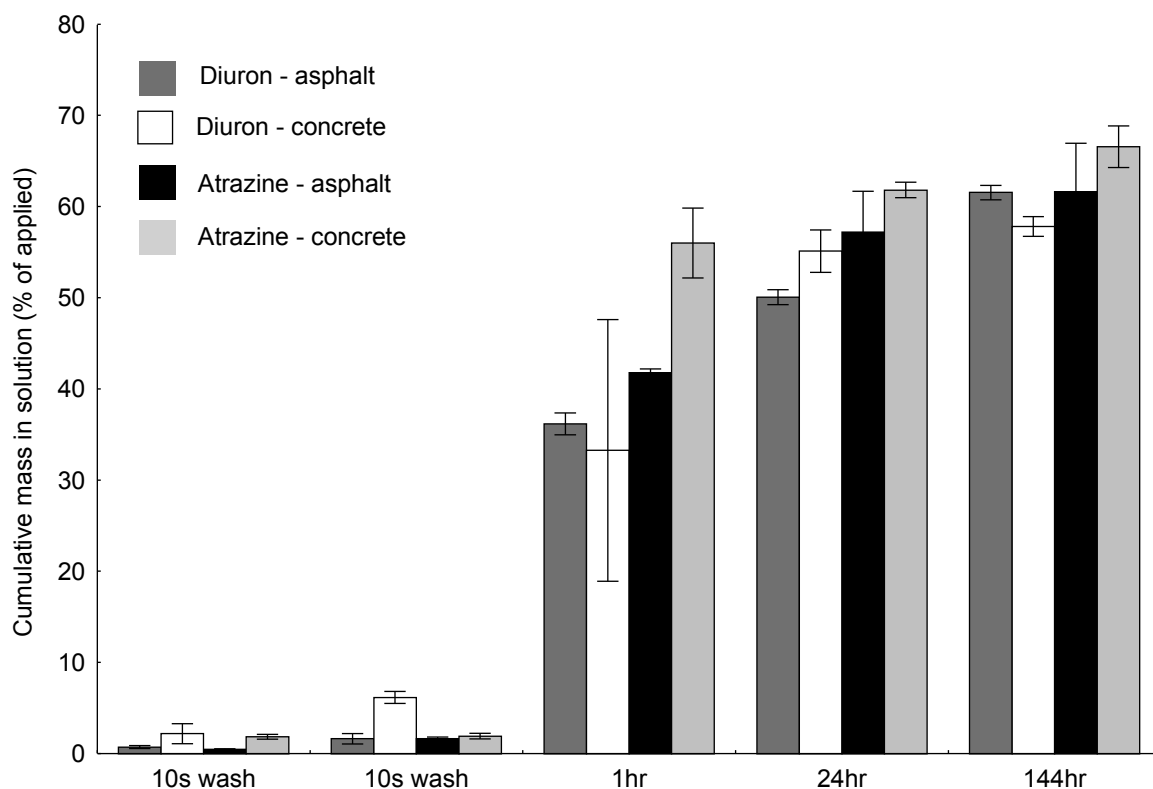


Figure 11 Diuron and atrazine loss from concrete and asphalt following spray application

4. DISCUSSION

Ordinarily, partition coefficients are quantified after sorption periods of 24 or 48 hours (OECD, 1998). At this time point, there is normally no change in the rate of partitioning. The experimental period for partitioning to herbicides was extended in the current study to enable significant differences to be measured, after accounting for variability between the replicates. The results demonstrated that there was a continuous decline throughout the 144 hours. Although it is possible that further partitioning may have occurred after 144 hours, the time period given for sorption to occur was not extended for practical reasons. In general, therefore, herbicide partitioning to hard surfaces is much more limited than in soils, but the process does occur and the extent of the significance of the partitioning varies between surface types.

Herbicide partitioning to asphalt was noticeably greater than to concrete or granite ballast. This could be expected given that asphalt contains a significant source of hydrocarbons, in the form of bitumen, and it is known that herbicides partition to organic carbon. Indeed, the existence of a strong relationship between the measured K_p for asphalt and literature-values of K_{oc} indicates that the sorption kinetics are likely to be similar between asphalt and soils. It is probable that sorption accounts for the lower losses of the majority of herbicides from asphalt than concrete in the controlled washoff study (Shepherd & Heather, 1999).

However, as occurs in the soil environment, physical processes may also be of importance. Despite similar volumes of water being used in the desorption and controlled washoff studies (16.7 mm of equivalent rainfall and 15 mm of rainfall respectively), herbicide removal was greater in the desorption study for both surface types and both compounds (Figure 12). In the controlled washoff study water flowed across the surface of each slab, and solution could have been retained by gravity in the micro-topological depressions. Conversely, in the desorption study surfaces were upturned when exposed to the clean water. The inability for solution to be physically retained on the surface in the desorption study may partly explain the greater quantity of herbicide removed from the surfaces. Moreover, the difference in results between the two studies was most noticeable for asphalt, the surface of which is more pitted than concrete, further supporting the theory of physical retention.

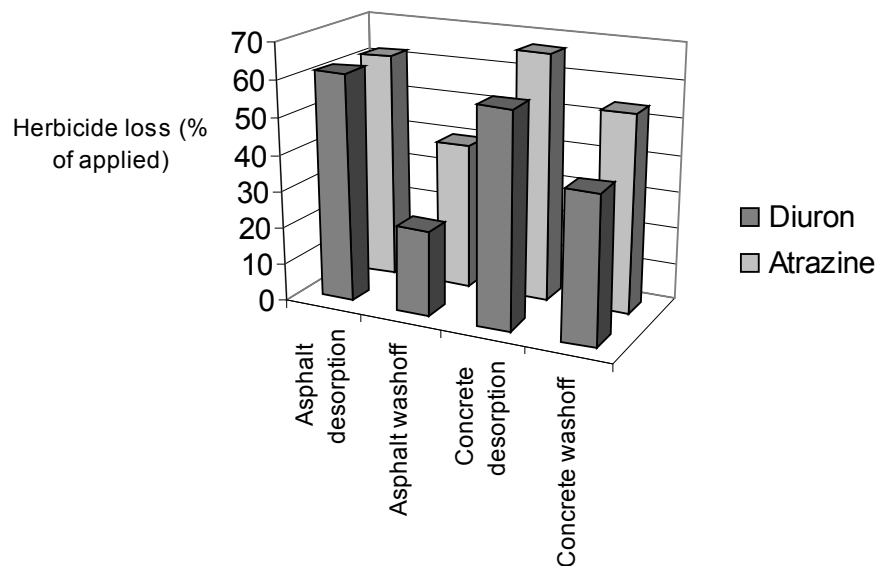


Figure 12 Comparison of herbicide loss from the current desorption study and previous controlled washoff study (Shepherd & Heather, 1999)

There was relatively little partitioning to concrete, and the relationship between the measured K_p and literature-values of K_{oc} was weaker than for asphalt. This indicates that the sorption kinetics differ between soils and concrete which is to be expected given the relative absence of an organic carbon content of concrete. However, other fractions of the soil can be involved in partitioning, including the clay and/or mineral fractions, but to a much smaller extent (Karickhoff, 1984). It is probable that the processes governing partitioning to the non-organic matter fractions in the soil are similar to those occurring between herbicides and concrete, due to the absence of organic matter in concrete. These processes tend to be more physical and dependent on factors such as pH, thus the factors affecting herbicide partitioning to concrete may vary depending on the compound. For example, there was no measurable partitioning of dichlorophen to concrete even though there was significant partitioning to asphalt. The partitioning of oryzalin to concrete was also lower than could be expected based on its partitioning to asphalt. Both dichlorophen and oryzalin are weak acids and have pKas near the range of the pH of the solution when exposed to concrete. (pKa = 7.6 and 11.6 for dichlorophen and 9.4 for oryzalin; pH of water with concrete = 8.7). It is possible that these compounds were dissociated when in solution, thus there was only a limited quantity of the compound available for partitioning during the course of the experiment. Isoxaben also had a lower K_p for concrete than could be expected given its K_p for asphalt, even though isoxaben does not dissociate to any significant extent; a similar behaviour was observed in the controlled washoff study where isoxaben removal from concrete as a percent of that applied was higher than oryzalin, diuron and atrazine indicating that there is a process inhibiting the retention of isoxaben on concrete. However, this does not necessarily translate to

isoxaben being an unfavourable compound to use on hard surfaces because the rate of application is relatively low, thus the actual mass of isoxaben removed from the surface will also be low.

Another possible explanation for the observed behaviour of the different compounds is the physical translocation into the matrix of the concrete. Concrete can hold approximately 8% of its own weight in water (Ohdaira and Masuzawa, 2000), and it was observed that, when the concrete was placed in the solution, some solution would move up the side of the block. It is possible that both the molecular weight and the solubility of a compound would influence the extent to which translocation contributes to the sorption process. Isoxaben and oryzalin both have relatively low solubilities and high molecular weights (1.42 and 2.6 mg L⁻¹ and 332 and 346 respectively) which could reduce their ability to be translocated within the matrix, hence the lower than 'expected' partitioning to concrete. Sorption of oryzalin to concrete was enhanced when the surface was pre-heated to 30°C which may be due to the ability of the drier concrete to uptake more water. However, the influence of translocation within the matrix of concrete may be more significant when herbicide is applied by spraying when water volumes used are relatively low, as the high water volumes used in the sorption study may mask any potentially larger differences. It is probable that a number of processes dictate the extent to which a compound partitions to concrete and the influence of the each process may depend on the physical of the compound in question.

Other evidence to support the theory of the importance of physical processes in influencing herbicide loss from hard surfaces is the comparison of the sorption and desorption results. For example, in the desorption study 67% of the initial mass sprayed onto the surface of concrete was recovered, but only 7% of that that was not recovered may be partitioned giving an 'unexplained' loss of 26% (Table 3). There were similar non-sorption losses from asphalt and for diuron indicating that other processes contribute to herbicide retention to hard surfaces, although it is acknowledged that some of the apparent non-sorption losses may be a factor of the natural variability between replicates and the analysis of the solutions.

	Sorbed		% of initial mass 'Desorbed'		Unexplained loss	
	Asphalt	Concrete	Asphalt	Concrete	Asphalt	Concrete
Atrazine	13	7	62	67	25	26
Diuron	26	12	62	58	12	30

Table 3 Comparison of results from the sorption and desorption studies

The negligible partitioning of fluoranthene and phenanthrene to granite ballast was unexpected given that in the controlled wash-off study (Shepherd & Heather, 1999) there was greater retention of

herbicides to granite ballast than to concrete or asphalt. In the current study, the ballast was washed with water to remove any dust, but in the controlled washoff study, whilst the ballast was new it was not washed and therefore contained rock dust, thus it can be inferred that any herbicide retention that occurred in the washoff study was due to the presence of the dust and not the granite rock itself. Due to the minimal sorption of compounds with high K_{oc} s to granite ballast and the absence of any partitioning of atrazine and diuron, experiments with ballast were discontinued. However, an additional study was conducted to assist in describing the movement of herbicides through railway ballast. These findings are reported separately (Ramwell, 2002).

Considering the pattern of herbicide loss, the results of the 'desorption' study support the findings of the controlled wash-off study and the roadside study where losses at the onset of rainfall formed a significant proportion of the total loss during the experimental period. In the desorption study, more than half of the available atrazine or diuron was removed within the first hour of being exposed to clean water and this was as much as 84% for atrazine loss from concrete. After just two sequential 10-second washes in clean water, 7% of the applied diuron was removed from concrete. When the surfaces that had been exposed to a herbicide solution were removed to clean water, some of the compound was also recovered. Approximately 7% of the final atrazine mass sorbed to asphalt was recovered after 1 hour when the test surface that was exposed to the herbicide solution was removed to clean water. After being in contact with water for 144 hours approximately 40% of the sorbed atrazine was recovered. This compares to a total recovery of only 3% from concrete. It is unlikely that in reality hard surfaces would remain in continuous contact with water for such a length of time, but the temporary sorption of atrazine may result in low levels of the herbicide being entrained in runoff with each sequential rainfall event. These patterns of herbicide loss may be of importance with regard to environmental exposure.

As a means of quantifying the partition coefficient of a compound to asphalt and concrete, the experimental protocol could easily be undertaken by any laboratory without the need for specialist equipment. The method therefore lends itself as being suitable to be adopted as standard. The variability observed between the replicates demonstrates the need for such replication, and it would be advisable to use a minimum of three replicates. In addition, it would be advisable to repeat the test on different occasions and/or with different initial concentrations to ensure any natural variability is encompassed. The current study has shown that the experiment can be undertaken satisfactorily at room temperature although the apparatus should be kept in the dark. The initial temperature and moisture content of the test surfaces does not significantly affect partitioning after 144 hours. However, it is good practice to ensure that the starting conditions are always equal. This can be achieved by moving the test surfaces into the room in which the experiment will be conducted at least 24 hours prior to the study being undertaken to bring the temperature and moisture content of the

surfaces in line with that of the ambient conditions. Although there were only minor differences between results for the technical grade and product, the test should be performed on the active substance and not the formulated product to prevent the introduction of unknown variables.

When using the measured K_p for predicting the behaviour of herbicide loss following application, it should be remembered that the results are only as accurate as the data used in the prediction and account of variability should be made for. The same applies should the K_p be predicted from the literature-value of K_{oc} using the relationship illustrated in Figure 10. It was noted during the literature search that there was variation in the K_{oc} values given. This is to be expected given the uncertainty surrounding octanol-water partition coefficients (Renner, 2002). Consequently, although there was variability in measured K_p , this should not devalue its use as variations were relatively small compared to those observed in the literature-values of K_{oc} . The appropriate course of action may be to use the range of K_{oc} values given to predict a range of environmental concentrations. Although the relationship between K_{oc} and K_p for concrete was not strong, the actual quantity of partitioning was also not great thus other physical processes may be of more importance in influencing herbicide loss from concrete and these factors are accounted when the values of K_p are used in the Tier-1 model (Hollis, 2002).

Herbicide removal from sprayed surfaces was infinitely more time consuming than conducting the sorption study, and there was more room for error due to losses during spraying – a factor that may vary between the replicates. Although it would be inadvisable to use this method as a measure of ‘sorption’, the method is less time consuming than conducting a controlled wash-off study, thus the laboratory-scale desorption protocol could be used to investigate factors such as the effect of different formulations.

5. CONCLUSIONS

- Herbicides will partition to asphalt and there is an exponential relationship between the K_{oc} of a compound and the K_p for asphalt.
- Herbicide partitioning to concrete is very limited and it depends on the physical characteristics of the compound.
- There was no significant partitioning of herbicides to granite ballast.
- Physical processes are probably more significant to describing herbicide loss from a hard surface than occurs in the soil environment.
- The majority of herbicide available for removal is lost within the first hour of being exposed to water.
- 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.
- The measured K_p are valuable data for improving the performance of the Tier-1 hard surfaces risk assessment model.

6. ACKNOWLEDGEMENTS

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Appendix 1 Method development

Introduction

A previous investigation into glyphosate partitioning to hard surfaces (Sinclair *et al.*, 2002) used plastic tubs as the apparatus for conducting the experimental work. Plastic was used in preference to glass due to the commercial availability of plastic tubs and because glyphosate, unlike most pesticides, does not readily bind to plastic. The majority of pesticides, particularly those with high K_{ow} s, could be expected to adsorb to plastic. However, the extent of potential adsorption was not known and may have been within acceptable error margins. A simple study was conducted using fluoranthene ($\text{Log } K_{ow} = 4.95$) to investigate the possibility of using plastic materials.

Method

A litre of distilled water was poured into a 3-litre plastic tub and 100 ng of fluoranthene added. The solution was stirred for five minutes using a magnetic bar and stirrer after which a sample (1 ml) was taken. Asphalt and concrete slabs (0.015 m^2) were glued to the lids of the tubs such that when the lids were placed on the tubs the surface area was exposed to a depth of 3 mm. In addition to the slabs, two controls were used; one where the tub contained fluoranthene but no slab and another containing an asphalt slab but no chemical in the distilled water. All tests were replicated three times. An aliquot (1 ml) of solution was taken after 2, 6, 24, 48 and 96 hours. All samples were stored in glass vials at 4°C prior to analysis. Samples were analysed by HPLC.

Results

Within 2 hours, the mass of fluoranthene in solution had approximately halved, and after 6 hours, the remaining concentration was close to the detection limit (Figure 13).

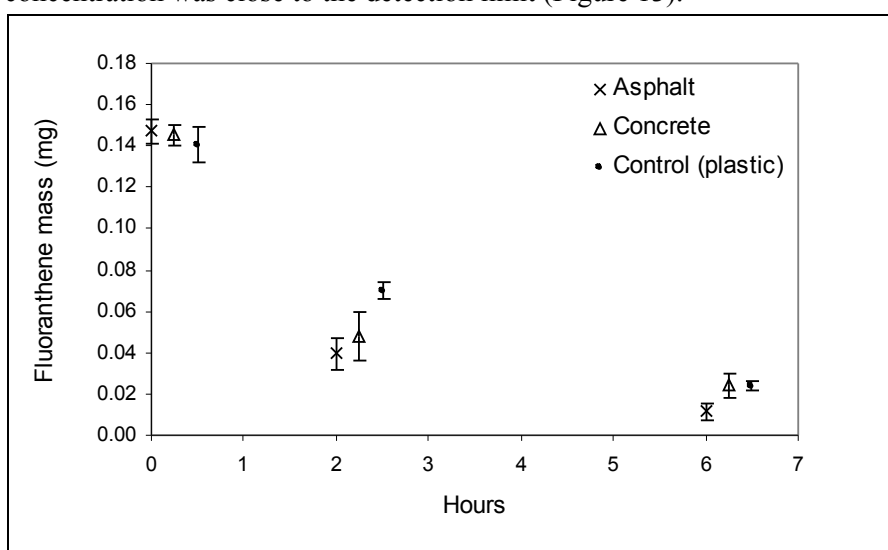


Figure 13 Fluoranthene mass after exposure to asphalt and concrete slabs in plastic containers

Discussion

Due to the rapid partitioning of fluoranthene to all exposed materials and the low concentrations remaining in solution, samples taken after 6 hours were not analysed. Although fluoranthene does partition to plastic, there was a significant difference between the control and the asphalt indicating that there was also partitioning to the asphalt. After 2 hours, there was a significant difference between concrete and the control but this was not apparent after 6 hours.

Conclusion

Fluoranthene rapidly partitions to asphalt, concrete and plastic. Plastic is not suitable for use with chemicals of high K_{ow} . Hard surfaces do have the ability to sorb organic compounds, particularly asphalt.

Reference

Sinclair CJ, Ramwell CT and Shepherd AJ (2002). Cranfield Centre for EcoChemistry research report (unpublished).

Appendix 2 Concentration of compounds

	Concentration (mg L ⁻¹)		
	Label-application	Solubility	Used for standard test
Fluoranthene	n/a	0.26	0.1
Phenanthrene	n/a	1.15	0.1
Atrazine	18	32	18
Diuron	16.2	36.4	16.2
Oryzalin	10.4	2.6	2
Oxadiazon	27	1	27
Isoxaben	0.45	1.4	0.45
Dichlorophen	36	30	28

Appendix 3 Temperature effect

To establish the conditions necessary to raise the surface temperature of asphalt and concrete to *c.* 30° C, slabs were placed in the oven at 70°C for 1 hour. The surface temperatures of three concrete and three asphalt surfaces were noted using a leaf temperature probe (Delta-T devices, type MT2) prior to and following heating. The weight of the slabs was noted prior to and following heating as it was anticipated that there could be some moisture loss during heating. After one hour at 70°C the average temperature of a concrete block was 40°C and 42°C for an asphalt block, and the weight of the

concrete blocks had decreased by 1 g whereas there was no noticeable change in that of the asphalt blocks.

The experiment was amended to the conditions of 50°C for 30 min and conducted a total of three times. The surface temperature of both the asphalt and concrete blocks following heating was 30 ±2°

C. The blocks decreased in weight by less than 0.5 g.

Appendix 4 Summary of experiments

Compound		Surface under investigation			Conc. of solution (mg L ⁻¹)	Comment
		Asphalt	Concrete	Ballast		
Fluoranthene	Technical grade	✓	✓	✓	0.1	Method development
Phenanthrene	Technical grade	✓	✓	✓	0.1	Extend range of K _{ow}
Atrazine	Product*	✓	✓	✓	18	Formulation effect
Atrazine	Technical grade	✓	✓	✓	18	Standard test
Diuron	Product*	✓	✓	✓	16.2	Formulation effect
Diuron	Technical grade	✓	✓	✓	16.2	Standard test
Diuron	Technical grade	✓	✓	x	16.2	Repeatability of method
Diuron	Technical grade	✓	✓	x	5.4	Concentration effect
Diuron	Technical grade	✓	✓	x	10.8	Concentration effect
Diuron	Technical grade	✓	✓	x	16.4	Concentration effect
Oxadiazon	Product*	✓	✓	x	27	Formulation effect
Oxadiazon	Technical grade	✓	✓	x	27	Standard test
Oryzalin	Technical grade	✓	✓	x	2.0	Standard test
Oryzalin	Product*	✓	✓	x	2.0	Formulation effect
Isoxaben	Technical grade	✓	✓	x	0.45	Standard test
Oryzalin	Technical grade	x	✓	x	2.0	Different concrete types
Diuron	Technical grade	x	✓	x	16.2	Different concrete types
Oryzalin	Technical grade	x	✓	x	2.0	Temperature effect
Oryzalin	Technical grade	✓	x	x	2.0	Temperature effect
Diuron	Technical grade	x	✓	x	16.2	Moisture effect
Diuron	Technical grade	✓	x	x	16.2	Moisture effect
Oryzalin	Technical grade	✓	✓	x	2.0	Fridge vs lab
Diuron	Technical grade	✓	✓	x	28	Repeat concentration effect
Dichlorophen	Technical grade	✓	✓	x	28	Extend range K _{ow}
Isoproturon	Technical grade	✓	✓	x	15	Extend range K _{ow}
Atrazine	Technical grade	✓	✓	✓	4.5 mg	Spray-applied desorption
Diuron	Technical grade	✓	✓	x	4.05 mg	Spray-applied desorption
Oxadiazon	Technical grade	✓	✓	x	22.5 mg	Spray-applied desorption

*Atrazine = MSS Atrazine, Diuron = Freeway, Oryzalin = Surflan, Oxadiazon = Zapper

Appendix 5 Literature values of K_{oc}

	Koc	Koc used	Data source
Fluoranthene	41700	41550	Chemfate
	41400		Chemfate
Phenanthrene	23000	11979	Chemfate
	4365		Chemfate
	5248		Chemfate
	8318		Chemfate
	10000		Chemfate
	18800		Chemfate
	14125		http://wlapwww.gov.bc.ca/wat/wq/BCguidelines/pahs/pahs-01.htm
Atrazine	106	113	Lewis & Tzilivakis, 2000
	118		Brown <i>et al.</i> , 2000
	100		Manufacturer
	99		Chemfate
	172		Chemfate
	49		Chemfate
	149		Chemfate
Diuron	477	334	Lewis & Tzilivakis, 2000
	218		Brown <i>et al.</i> , 2000
	150-500		Manufacturer
	162		Chemfate
	380		Chemfate
	389		Chemfate
	398		Chemfate
Dichlorophen	4103	4100	Lewis & Tzilivakis, 2000
	4098		Brown <i>et al.</i> , 2000
Isoxaben	1400	1400	Manufacturer
	1457		US EPA
	1442		US EPA
	1453		US EPA
	767		Brown <i>et al.</i> , 2000
	1400		Lewis & Tzilivakis, 2000
Isoproturon	154	147	Lewis & Tzilivakis, 2000
	140		Brown <i>et al.</i> , 2000
Oryzalin	700-1100	756	Tomlin, 2000
	625		Brown <i>et al.</i> , 2000
	700-1100		Manufacturer
	600		extoxnet

Extoxnet <http://pmep.cce.cornell.edu/profiles/extoxnet>

Chemfate: <http://esc.syrres.com>

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