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2. Effect of time interval between application and first precipitation event

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Duurzaam Onkruid Beheer op verhardingen

Note 353

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Note 353

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Table of contents

Summary

About 75% of the municipalities in the Netherlands use herbicides to control weeds on hard surfaces. A negative side-effect of the use of herbicides on hard surfaces is the emission of these herbicides to surface waters which may cause problems for the quality of surface water and for the drinking water production. Use of herbicides on hard surfaces represents a small part of the total use of herbicides in the Netherlands but contributes for a substantial part to the total emission to surface waters. Glyphosate, admitted for chemical weed control on hard surfaces in the Netherlands, is most commonly used for chemical weed control on hard surfaces.

Weather conditions before and after spraying herbicides are assumed to be of key importance for the extent of runoff of herbicides. The aim of the experimental work is to determine if precipitation shortly after application results in more runoff of glyphosate than periods that are longer. Because the climate can not be manipulated, and an unexpected natural rain shower would interfere in the experimental setup, the experiment was split up in two separate tests. Two factors affect the runoff in the rain shower:

1. Wetness of the brick-soil system; runoff from a wet system is greater than runoff from a dry system. When the period between application and the rainfall increases, also the dryness of brick-soil system increases. So, a longer period between application and rainfall can lead to less runoff because of increased dryness of the system.
2. Dissipation; in the period between application and rainfall dissipation processes decrease the amount of glyphosate on/in the bricks.

To determine the impact of these two factors separately, two tests were done. Firstly, a plot experiment to determine the impact of the moisture content of the brick-soil system. Secondly, a dissipation experiment in which glyphosate was applied on pieces of foil and on single bricks, to assess the impact of dissipation processes.

The outdoor plot experiment was carried out under controlled conditions in two series, respectively on 3 and 17 June 2003. The experiment had 2 alternatives; determining runoff from (a) relatively dry and from (b) relatively wet brick-pavement. In the dry plot alternative, the plot was kept dry for at least 3 days before carrying out the experiment. In the wet plot alternative the plot was artificially irrigated before spraying. Each alternative had 2 replicates. In the experiment runoff water was collected and analysed for glyphosate. Also the moisture content of the soil below the brick pavement before and after the experiment was determined.

In the dissipation experiment the dissipation of glyphosate was measured from bricks that were identical to the bricks in the experimental plots. Glyphosate was sprayed at the individual bricks. The brick surfaces were extracted with water at approximately 3, 72 and 168 hours after applying the glyphosate product.

In the plot experiment in the first series, the amount of glyphosate in runoff water relative to the amount applied on the plot was similar for both plots (respectively 18% for the dry plot and 17% for the wet plot). In the second series, glyphosate runoff was remarkably higher for the dry plot (14%) compared to the wet plot (9%).

In the dissipation experiment after 3 hours 24% of the glyphosate mass applied on the bricks was recovered. After 72 and 168 hours, 17% and 18% of applied glyphosate mass was recovered from the bricks.

In this study, a wet pavement did not result in increased runoff of glyphosate in comparison with a dry pavement. In two series, glyphosate runoff was respectively similar and higher from the dry brick pavement than from the wet brick pavement. The difference in infiltration capacity of the soil under the pavement may have caused the difference between the two plots, and not the moisture conditions of the pavement. The infiltration capacity of the soil under the plot that was kept dry, was possibly lower than that of the plot that was wet. So, water starts to flow over the surface of the dry pavement in an earlier stage compared to the wet pavement.

With the dry pavement it was intended to mimic the longer period between the application and the first rain shower; the wet pavement then being the situation with a rain shower shortly after application. Because the plot for the dry situation and the plot for the wet situation differed too much, the effect of the wetness of the hard surface could not be determined. Other factors, possibly the infiltration capacity of the soil below the bricks determined the infiltration of water and glyphosate and therefore also the runoff.

In the dissipation experiment in which the extraction of glyphosate from bricks was tested showed that 3 hours after application 24% could be extracted, which percentage only slightly decreases in the period up to one week thereafter. So, after the initial reduction of availability of glyphosate, its availability appears to reduce only slowly in the course of time. Hence, dissipation processes in the time period between the application and the first rain shower hardly reduce the potential runoff of glyphosate, on the basis of this test.

It is recommended to further study the impact of initial infiltration rates of pavements on runoff, and study the possible release in time of glyphosate from different types of hard surface material.

Preface

This research was carried out within the project 'Rational Weed Management on hard surfaces' in the period June 2003. VEWIN (the Dutch association for drinking water producers) and Monsanto Europe have taken an initiative in 2000 that aims at a substantial reduction of emission of herbicides from hard surfaces to surface waters. At the end of 2001, ZHEW (Waterboard Hollandse Eilanden en Waarden) joined the initiative. The initiative has lead to a project named 'Rational Weed Management on hard surfaces' running from 2002 up to 2005. The objective of the project is the development, testing and securing of a system of integrated weed control on hard surfaces through which the runoff of herbicides and the formation of their metabolites is reduced to an acceptable level below the legal standard. The project leads to a Decision Support System (DSS). In the DSS, policy makers, owners of hard surfaces, managers and contractors can find information on weed control methods and their side effects and on prevention of weed growth. Furthermore, the DSS will advice not to apply herbicides on parts of hard surfaces if the risk of herbicide runoff is considered too high. Plant Research International is the contractor and co-ordinator of the project, Alterra and CLM (Centre for Agriculture and Environment) are subcontractors in the project.

In this research the effect of moisture conditions of hard surfaces on emission of herbicides from hard surfaces was quantified. In addition the dissipation of glyphosate applied on brick-pavement is determined in time. The outdoor experiment was carried out on 3 and 17 June 2003. In previous research the effect of a buffer zone around drains of sewage systems on glyphosate runoff was tested experimentally (Luijendijk *et al.*, 2003).

We would like to thank VEWIN, Monsanto Europe and ZHEW for supporting this study and those who have commented on this report.

1. Introduction

About 75% of the municipalities in the Netherlands use herbicides to control weeds on hard surfaces. The main reason for using chemical weed control is the high efficiency. A negative side-effect of the use of herbicides is the emission of these herbicides from hard surfaces to surface waters which can cause problems for aquatic eco-systems and for the production of drinking water from surface water. Water boards and drinking water companies in the Netherlands frequently detect pesticides and their metabolites in surface water. Use of herbicides on hard surfaces represents a small part of the total use of herbicides (in kilograms) in the Netherlands but contributes a substantial part to the emission to surface waters. In the Bommelerwaard for example, the use of herbicides on hard surfaces contributed 75% of the emission to surface waters whereas the use on hard surfaces represented only 1% of the total use of herbicides in that area (Merkelbach *et al.*, 1999).

Glyphosate, admitted for chemical weed control on hard surfaces in the Netherlands, is most commonly used for chemical weed control on hard surfaces at present. The legal standard for all pesticides and their metabolites in water to be used for the production of drinking water is 0.1 μg/L. The Maximum Admissible Risk Level (MAR) in surface waters for glyphosate is 77 μg/L (ad hoc).

This research was carried out to test measures that should reduce the runoff of glyphosate to surface water whilst applying a glyphosate formulation to hard surface. In the first part of this research it was shown that a buffer zone around the drains, where no glyphosate is applied, can reduce the runoff (Luijendijk *et al.*, 2003). In this second part of the research the effect of taking into account the weather forecast in choosing the time of glyphosate application is studied. The proposed measure tested here is the restriction not to apply glyphosate when rain is expected within 24 h after the planned glyphosate application.

The aim of the experimental work is to determine if precipitation shortly after application results in more runoff of glyphosate than periods that are longer. Because the climate can not be manipulated, and an unexpected natural rain shower would interfere in the experimental setup, the experiment was split up in two separate tests. Two factors affect the runoff in the rain shower:

1. Wetness of the brick-soil system; runoff from a wet system is greater than runoff from a dry system. When the period between application and the rainfall increases, also the dryness of brick-soil system increases. So, a longer period between application and rainfall can lead to less runoff because of increased dryness of the system.
2. Dissipation; in the period between application and rainfall dissipation processes decrease the amount of glyphosate on/in the bricks.

To determine the impact of these two factors separately, two tests were done. Firstly, a plot experiment to determine the impact of the moisture content of the brick-soil system. Secondly, a dissipation experiment in which glyphosate was applied on pieces of foil and on single bricks, to assess the impact of dissipation processes.

Glyphosate runoff is expected to be higher when the moisture content of the brick-soil system is higher through rainfall previous to the application of herbicides. When the brick-soil system is dry, more infiltration of runoff water containing glyphosate is expected. Infiltration of runoff water and herbicides in brick-pavement and soil reduces runoff (Beltman *et al.*, 2002, Beltman *et al.*, 2001). An outdoor experiment was carried out under controlled conditions to quantify the effect of moisture conditions of hard surfaces on glyphosate runoff via, a wet versus a dry brick-soil system,. Each alternative had two replicates. In addition the dissipation of glyphosate applied on single bricks under dry conditions is determined in time. A dry period between the application of herbicides and succeeding precipitation is expected to reduce emission of glyphosate. In this period glyphosate can dissipate (by e.g. irreversible binding or (photo)transformation), dependent on the length of the in-between period. To be able to distinguish between dissipation from the bricks and absorption of glyphosate to the bricks, the dissipation test is also done with an inert material (polyethene foil).

In chapter 2 the set-up of the experimental work is elaborated. The results are presented in chapter 3 and discussed in chapter 4. Conclusions and recommendations are given in chapter 5.

2. Material and Methods

An outdoor experiment was carried out to gain a better insight in the runoff of glyphosate from hard surfaces. The experiment had 2 alternatives; determining runoff from (a) wet and from (b) dry brick-soil systems. In the wet plot alternative the plot was artificially irrigated before applying glyphosate. In the dry plot alternative, the plot was kept dry for approximately 3 days before carrying out the experiment. Each alternative had 2 replicates.

In section 2.1 the set-up of the experiment and in section 2.2 the dissipation of glyphosate applied on brick-pavement is described. Section 2.3 elaborates on the laboratory analysis of the runoff water samples.

2.1 Outdoor experiment

2.1.1 Description of the plot

The alternatives (dry and wet brick-soil system) of the experiment were carried out on two separate, comparable plots with a distance between them of approximately 10 meters. The first series of alternatives were carried out on June 3 and replicated on June 17 2003. The wet alternative has been carried out twice on the same plot and so has the dry alternative. In the protocol the alternatives were meant to be switched between plots to level out the variation between the underground of the two plots. For a description of the selection criteria of the experimental site, see Luijendijk *et al.* (2003). The dimensions of the plots were 9 m x 11 m (99 m^2). Before the experiment, the plot was swept and weeds were removed. The plot was staked out with plastic foil filled with sand to make sure that during irrigation, the water deposit outside the plot would not get into the plot.

To simulate the precipitation pattern of rainfall as adequate as possible, an irrigation installation for horticulture was used. The installation consists of 4 PVC-tubes with a length of 10 m each. Each tube had 5 so-called 'Dan sprinklers type 8966' placed at intervals of 2.5 m. Each sprinkler deposited maximally 2 L/min. The tubes were placed in the plot with an interval of 2.5 m and were positioned approximately 25 cm above the soil surface.

At the lower side of the plot the drain was situated in the middle (Figure 1). In this drain the runoff was intercepted and pumped by a submerged pump to containers with a 25 L content.

2.1.2 Application of glyphosate

Glyphosate was applied with a portable band spraying device with six 1.6 mm Birchmeier cone nozzles with 0.6 mm diameter. The 6 nozzles together had a spraying width of 1.98 m. The plot was sprayed twice with perpendicular walking directions to obtain an equal distribution. The plot was sprayed in 5 lanes in length and in 4 lanes in width. Each lane started and ended approximately 0.75 meter outside the plot to prevent unequal distribution of glyphosate in the plot. These extra meters outside the plot were covered with plastic foil (1 m wide). This foil was removed after applying glyphosate to avoid potential contamination of the plot.

The distribution of the dose on the plot was verified by placing aluminium trays on the plot before spraying (Appendix I). Masses of glyphosate found in these trays were translated to kg/ha. The mean glyphosate dose in the aluminium trays on 3 June 2003 on the dry plot was 2.6 ± 0.5 kg/ha, this was on the wet plot 2.9 ± 0.2 kg/ha. On 17 June 2003 this was on the dry plot 2.7 ± 0.6 kg/ha and on the wet plot 3.8 ± 0.3 kg/ha. The spraying solution was prepared by adding 9.18 ml of Roundup Pro per L water. The real dose on the plot was calculated from the sprayed volume and the concentrations measured in the spraying solution. The dose was corrected for the 0.75-m-zone that was sprayed outside of the plot. The calculated doses on the plots are summarised in Table 1.

Table 1. Applied dose of glyphosate.

	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
dose on plot (g)	27.3	25.5	30.0	38.6
kg/ha	2.8	2.6	3.0	3.9

2.1.3 Experimental conditions and sampling

The experiment was carried out on 3 and on 17 June 2003. On 3 June, the wet plot was irrigated with approximately 10 mm of water, before spraying the plot with the herbicide. No rain fell for during the 3 days before the experiment, except approximately 2 to 3 mm rain on the day before. The dry plot was covered with plastic to protect it from the rain. The wet plot was additionally irrigated with approximately 10 mm water 4 h before the glyphosate application. On 16 June, one day before the applications, the wet plot was irrigated with approximately 21 mm of water. No rain fell during the 3 days before carrying out the experiment. The weather conditions were dry during the experiment.

After spraying, irrigation started after 3 hours. Details on irrigation are summarised in Table 2. Irrigation intensity was calculated from the irrigated millimetres of water derived from the volumes measured with a flow meter in the tube to the sprinklers and the duration of irrigation. The volumes were corrected for the irrigation deposited outside the plot, which was 29.4%, estimated from the spray distance of the sprinklers. Both experiments were carried out until 8 mm (equals 800 L on each plot) water had runoff into the drain and was collected in containers. In previous runoff experiments it has been shown that the highest glyphosate concentrations were found in the first mm of runoff water (Beltman *et al.*, 2001). Thereafter, concentrations decreased rapidly. Most of potential glyphosate runoff should take place within 8 millimetres.

Water running off into the drain was pumped into PVC containers (content 25 L) by a submerged pump (hard polythene and RVS). Of the first 100 L, one sample per container was taken (1 sample per 0.25 mm runoff water). Of the next 200 L one mixed sample per 50 L runoff water was taken. After 300 L was collected, mixed samples per 100 L runoff water were taken. In total 13 samples were taken for analysis (4 of 25 L, 4 of 50 L and 5 of 100 L). When a container was filled up with runoff water the time was registered. Also, every quarter of an hour the total volume pumped to the sprinklers was registered, to determine if the supply of water was constant. All samples were stored at 5ºC until analysis.

Table 2. Irrigation in the experiment.

	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
irrigation intensity (mm/hour)	11.1	12.2	12.3	11.9
duration of irrigation (min)	91.1	80.8	80.2	93.5

To monitor the distribution of water within the plot, 8 plastic trays were placed diagonally across the plot (Appendix II) (on 3 June, 7 instead of 8 trays were placed on the dry plot). These plastic trays with sharp edges were used instead of the pluviometers in former experiments (Luijendijk *et al.*, 2003) because of their larger interception capacity of water (low height and wide opening). The collected volume of water per plastic tray was translated to millimetres water. On 3 June, the mean collected millimetres of water in the plastic trays on the dry plot was 13.8 mm ± 4.2, on the wet plot this was 15.1 mm ± 4.1. Hence, the variation in distribution of water on the plots was more than 25%. On 17 June, the mean collected millimetres of water in the plastic trays on the dry plot was 14.6 mm ± 5.4, on the wet plot this was 18.0 mm ± 5.6. The variation in distribution of water on the plots was more than 30%.

2.1.4 Moisture content of the soil

Soil samples were collected to determine the moisture content of the soil before and after carrying out the experiment. Before every experiment 6 bricks were removed, in the proximity of the border of the plot, 3 on each side of the plot, at parallel height (see Figure 1). Samples of the 0-10 cm soil layer underneath these bricks were taken. Samples of the same height were mixed (total of 3 samples). After the experiment 6 bricks in the plot were removed and soil samples were taken. With these samples the increase in moisture content of the soil was determined.

The moisture content of the soil was determined by weighing the soil in an aluminium cup before and after placing it for a night in a stove by 105 °C. The moisture content in the 0-10 cm soil layer of the plot was calculated using the bulk density of the soil. The bulk density of the soil was estimated to be 1620 kg/m^3 (Luijendijk *et al.*, 2003).

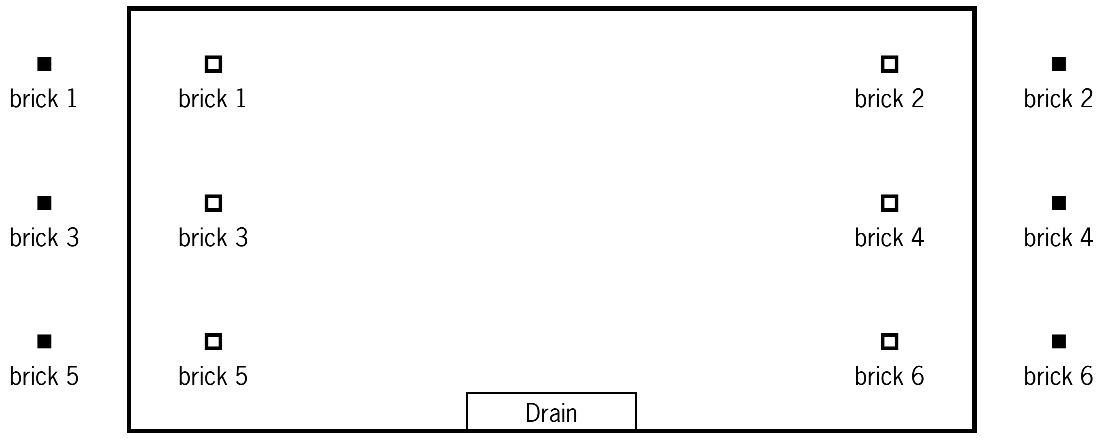

Figure 1. Positions of the bricks below which soil samples are taken (before experiment ■, after experiment □).

2.2 Dissipation of glyphosate

The dissipation of glyphosate from single bricks and from pieces of polyethene foil was tested.

Dissipation of glyphosate can take place through (photo)chemical, irreversible binding or microbial transformation and via volatilization. To determine dissipation of glyphosate applied on single bricks in time, 1 ml of spraying solution (183 ml Roundup Pro/L, equal to 66 mg glyphosate/L) was applied equally with a syringe on 15 clean bricks (11 x 22 cm) on 17 June 2003. Two samples of the spraying solution were taken to determine the glyphosate content. As a control, 1 brick was not treated with glyphosate. The brick surfaces were washed off with water after respectively 3, 72 and 168 hours after applying the glyphosate. Every point of time had 5 replicates. In the period between applying glyphosate and extracting, the bricks were put in the open air as much as possible to expose them to direct daylight.

To wash off the brick surface, the brick was attached upside down on a support (Figure 2), in such a way that the brick surface was pointing downwards and slightly sloping. This to limit absorption of water by the brick. The brick surface was extracted with 250 ml of water. The extraction water was collected in an aluminium tray. After this the water was transferred to a polyethene (PE) bottle and analysed on glyphosate content.

The bricks that were washed off 72 and 168 hours after glyphosate application were weighed before and after extraction. This to determine the water uptake of the bricks. An average 2% of the 250 ml water was absorbed per brick. The water uptake equals 1% of the brick weight (approximately 4 kg).

Dissipation of glyphosate applied on bricks was compared to the dissipation of glyphosate from an inert (non reactive) surface, polyethene (PE) foil. For this purpose, 1 ml of spraying solution (206 ml Roundup Pro/L, equal to 74 mg glyphosate/L) was distributed equally with a syringe on 9 sheets of foil (10 x 30 cm) on 3 June 2003. Two samples of the spraying solution were taken to determine the glyphosate content. As a control, 1 piece of foil was not treated with glyphosate. The surfaces of the foils were extracted with water after respectively 4.5, 72 and 168 hours after applying the glyphosate. Every point of time had 3 replicates. In the period between applying glyphosate and the extraction, the foil sheets were put in the open air as much as possible. To extract the foil surface, each foil sheet was put in a polyethene (PE) bottle and 200 ml of water was added. The bottle was shaken for 30 minutes, then the extract was analysed on glyphosate content.

The degree of exposure to direct daylight differs between the brick experiment and the foil experiment. At rainfall the foil surfaces were put in a greenhouse at a temperature of 25 – 35°C, the bricks were kept indoors in periods that rainfall could occur.

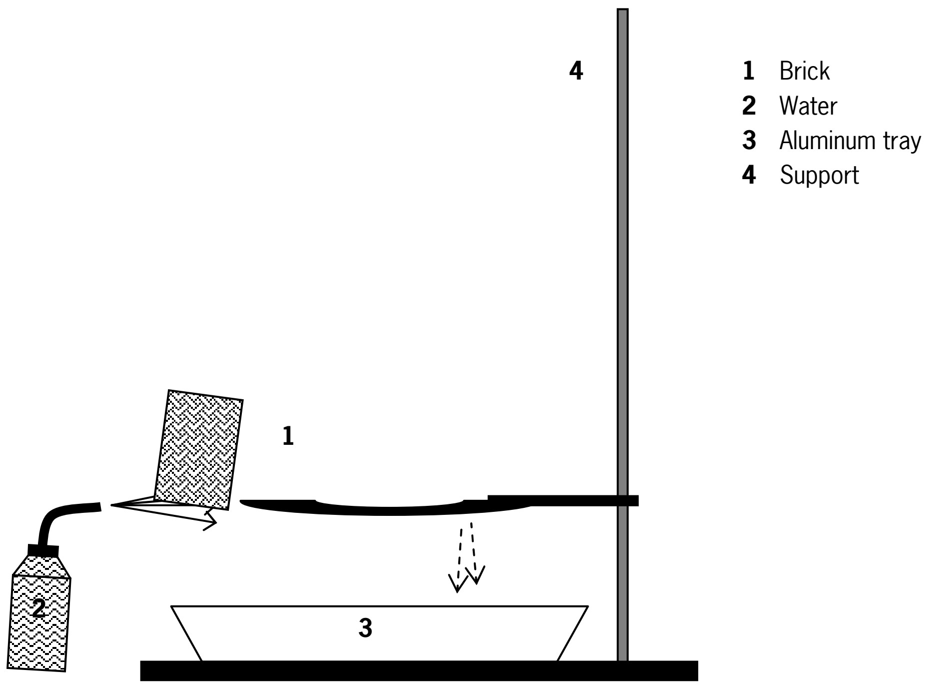

Figure 2. Brick extraction set-up.

2.3 Analysis of glyphosate

Glyphosate was measured on a HPLC-system with an online SPE-extraction unit (Prospect). This system uses HySpere-glyphosate SPE cartridges and a C40-glyphosate-column. Glyphosate was detected with a fluorescention detector (extinction at 265 nm, emission wave length 300 nm). The mobile phase was acetonitril/0.2% phosphoric acid (75/25 v/v%) 0.2% P-acid in what for a25%? . The samples were derivatised manually with fluoranylmethyl-chloroformate (FMOC) and pre-concentrated before analysis. The detection limit for glyphosate was 0.02 mg/L.

3. Results

3.1 Outdoor experiment

3.1.1 Water balance

For describing the water balance of the experiment, the irrigated and collected amount of water that were measured and the infiltration of irrigated water in the soil underneath the hard surface were estimated from the increase in moisture content in the soil.

In Table 3 the amount of water on the plot and the amount of water that had ran off to the drain, is summarised. Irrigation was continued until 8 mm (800 L) of runoff water was collected in containers. Table 3 shows that on 3 June it lasted 91 minutes on the dry plot to obtain 8 mm of runoff water and on the wet plot this took 81 minutes. On 17 June it took 80 minutes on the dry plot to collect 8 mm of runoff water, on the wet plot this took 94 minutes. The runoff percentage on the wet plot on 17 June 2003 was relatively low.

Table 3. Amount of irrigation and runoff water (mm).

	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
irrigation intensity (mm/hour)	11.1	12.2	12.3	11.9
duration of irrigation (min)	91.1	80.8	80.2	93.5
applied irrigation water (mm)	16.9	16.4	16.4	18.5
runoff to drain (mm)	8.0	8.0	8.0	8.0
runoff to drain (%)	47.3	48.8	48.8	43.2

The moisture content of the 0-10 cm soil layer of the plot, before and after the experiment, was determined (Table 4). The uptake of water by the soil was calculated by using the determined bulk density of 1620 kg/m^3. Irrigation increased the moisture content in the soil. The wet plots had a higher moisture content at start than the dry plots. On 3 June however, the differences regarding moisture content of the soil at starting point were small. On both dates the uptake of water by the wet plots was larger than by the dry plots, this was especially the case on 17 June 2003.

Table 4. Moisture content (mm) in soil layer 0–10 cm underneath the brick-pavement of the plot, before and after the experiment.

	Moisture content soil layer 0 –10 cm of the plot (mm)			
	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
before experiment				
mean	10.0 ± 0.8	10.6 ± 1.4	8.8 ± 0.7	11.0 ± 2.3
after experiment				
mean	13.0 ± 1.2	16.1 ± 0.7	11.6 ± 1.4	19.2 ± 3.4
increase (mm)	3.0	5.5	2.8	8.2

In Table 5 the water balance of the experiment is summarised. The amount of irrigation water on the plot was relatively high on the wet plot on 17 June 2003. The water balance is positive for all the plots, the remaining mm's of water were absorbed by the brick-pavement, evaporated or were transported below 10 cm depth.

Table 5. Water balance of the experiment.

	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
on plot (mm)	16.9	16.4	16.4	18.5
runoff to drain (mm)	8.0	8.0	8.0	8.0
increase in soil layer 0 – 0.10 m (mm)	3.0	5.5	2.8	8.2
not accounted for (mm)	5.9	2.9	5.6	2.3

3.1.2 Runoff of glyphosate

Concentrations of glyphosate in the runoff water samples are summarised in Appendix III. In Figure 3 and 4 the concentrations in runoff water are presented as a function of time. The cumulative runoff is the amount of water that ran off to the drain and was collected. On both dates, glyphosate concentrations in the first 1.5 mm runoff water from the dry plots were higher then from the wet plots.

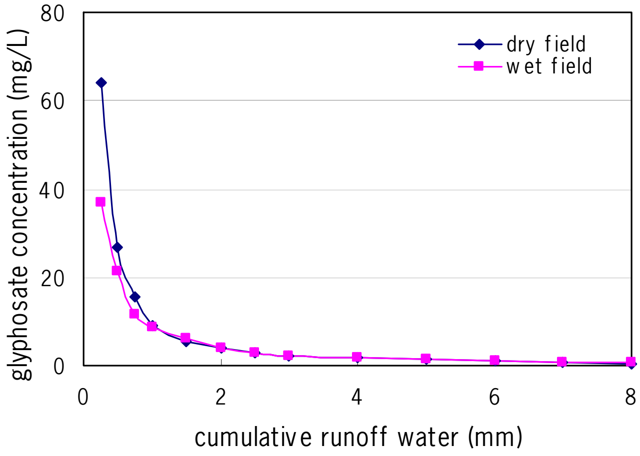

Figure 3. *Glyphosate concentration in runoff water, on 3 June 2003.*

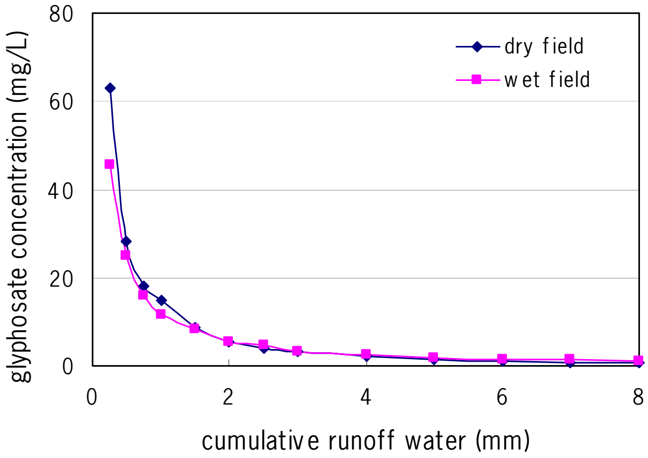

Figure 4. *Glyphosate concentration in runoff water, on 17 June 2003.*

Amounts of glyphosate in runoff water, expressed as percentage of the applied amount, were similar for the dry and wet plot on 3 June 2003 (see Table 6). Relative glyphosate runoff from the wet plot was remarkably low (8.5%) on 17 June 2003.

Table 6. *Glyphosate in runoff water relative to the applied amount of glyphosate on the plot.*

	3 June 2003		17 June 2003	
	dry plot	wet plot	dry plot	wet plot
applied on plot (g)	27.3	25.5	30.0	38.6
in runoff to drain (g)	4.8	4.3	4.2	3.3
runoff (%)	17.6	16.9	14.0	8.5

Cumulative masses of glyphosate as percentage of the applied amount are presented as a function of cumulative water runoff in Figures 5 and 6. The glyphosate mass was calculated by multiplication of the concentration of glyphosate in the runoff water sample with the runoff water volume collected (see 2.1.3).

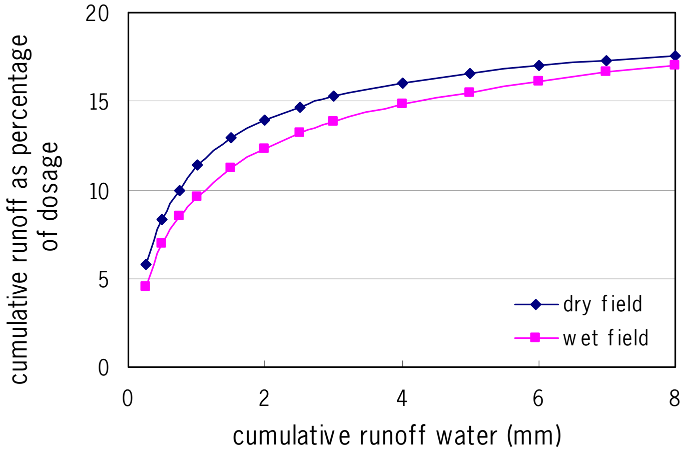

Figure 5. Cumulative glyphosate runoff relative to the glyphosate mass applied on the plot, on 3 June 2003.

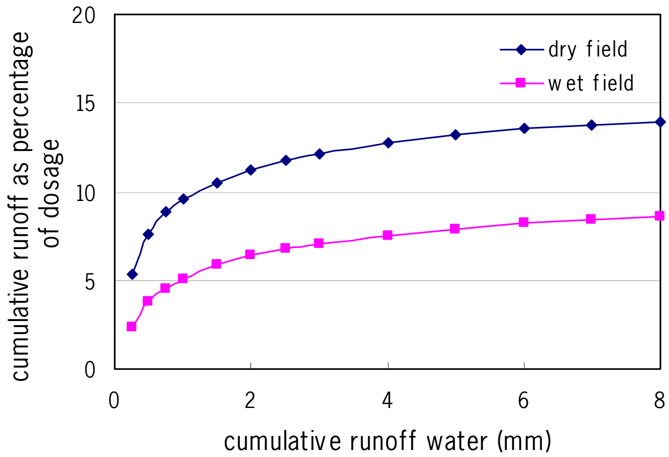

Figure 6. Cumulative glyphosate runoff relative to the glyphosate mass applied on the plot, on 17 June 2003.

3.2 Dissipation of glyphosate

The bricks were all dosed with the glyphosate formulation on 17 June 2003 at 16:00, and thereafter outdoors exposed to daylight. The sun was shining then, through a thin layer of clouds. So, the bricks were not exposed to intensive direct sunlight as occurring during the treatment of the plots around midday.

The first three bricks were extracted with water at 3 hours after the glyphosate application. The other bricks were exposed as much as possible to daylight outdoors. On 18 June 2003 this was direct sunlight during 6 hours. On 19 June the bricks were kept indoors because of rainy weather. The 3rd day they were exposed to the sun for 3 hours, before the 72-hour bricks were extracted with water. On the 4th and 5th day the remaining bricks were kept indoors. On the 6th and 7th day they were exposed to sunlight for 6 and 3 hours respectively, before they were extracted.

In Table 7, the recovery (glyphosate amount found in extracts relative to applied amount of glyphosate) is summarized. For the glyphosate extraction experiment on brick, the recovery found for the bricks that were extracted after 3 hours decreased only slightly thereafter, because after 72 and 168 hours the recovered fraction was almost the same.

Table 7. Recovery of glyphosate applied on brick.

treatment	recovery (%)
control (n=1)	0.0
3 hours (n=5)	24.1 ± 2.2
72 hours (n=5)	16.8 ± 3.6
168 hours (n=5)	18.1 ± 6.5

The polyethene foils were treated with the glyphosate formulation on 3 June 2003 at 15:30 and thereafter outdoors exposed to daylight. It was cloudy, so there was no direct sunlight, like during the treatments of the plots at the same day.

The first 3 foils were taken indoors 3.5 hours after the treatment and extracted with water 1 hour later. Because of the rainy weather they were only exposed outdoors on June 3. The rest of the period they were kept in the green-house, at temperatures between 25 - 35°C, but not exposed directly to uv-radiation.

In the glyphosate extraction experiment on foil, the recovery for extraction after 4.5 hours was higher than the recovery after 72 and 168 hours (Table 8). The recovery was equal for extraction after 72 and 168 hours. The relative difference in amount of extracted glyphosate between 4.5 hours and 72 hours was 36.6%.

Table 8. Recovery of glyphosate applied on polyethene foil.

treatment	recovery (%)
control (n=1)	0
4.5 hours (n=3)	97.2 ± 2.3
72 hours (n=3)	61.6 ± 3.8
168 hours (n=3)	61.2 ± 2.7

The recovery of glyphosate applied on foil was substantially higher than the recovery of glyphosate applied on brick (see Table 7 and 8).

4. Discussion

4.1 Outdoor experiment

Regarding the experiment, the estimation that 30% of the irrigated water deposited outside the plot is probably somewhat high. Calculations with spraying circles of an individual sprinkler with a radius of 3 and 3.5 m (observed) resulted in deposits outside the plot of respectively 27% and 29% of the irrigated water. So, the irrigation intensity on the plot was probably slightly higher. For a further discussion regarding the set up of the experiment see Luijendijk *et al.*, 2003.

On 3 June, the dry and wet plot showed similar runoff (see Fig. 5). The runoff from the wet plot was slightly less. A possible explanation for this similar result, when expecting that the wet plot would show more runoff than the dry plot, is that two independent processes may influence the effect: (1) the wet plot is more permeable than the dry plot, so the infiltration can be higher; (2) As the system of the wet plot is wet, the total infiltration is lower compared to a dry brick-soil system. The net result of these two processes may make runoff of glyphosate of the two plots similar. The water balance in Table 5 shows that the number of irrigated millimetres of water for the dry and for the wet plot to obtain 8 mm's of runoff is about the same. So, the similarity of the runoff of glyphosate seems to be caused by the hydrology.

On 17 June, the percentage of applied amount of glyphosate that ran off from the wet plot, 8.5%, was remarkably low compared to the dry plot, 14%. The increase in moisture content in the 0-10 cm soil layer was substantially higher in the wet plot compared to the dry plot on 17 June 2003 (respectively 8.2 and 2.8 mm). So, from these increases in moisture content, the infiltration of water on the wet plot seems to be larger than on the dry plot. Table 5 shows that on the wet field 2 mm of water extra had to be irrigated to obtain a runoff of 8 mm. To collect 1 mm of runoff it took 13¼ minutes at the dry plot and 16½ minutes at the wet plot, whilst the irrigation rate differed hardly in this period. This indicates that the permeability of the wet plot is higher than from the dry plot.

Although planned differently, the wet plots have been carried out twice on the same plot; so have the dry plots. It is possible that the brick pavement and soil of the wet plot were more permeable to water than that of the dry plot. That could explain the higher infiltration of water in the wet plot.

The plot experiment in which one plot was wet and the other dry, has two replicates. From the runoff water from wet plots replicate it can be concluded that the experiment can be replicated sufficiently on the same plot. The amount of runoff water from the wet plots is about the same in the replicates. the replicates of the dry plot show the opposite. The water runoff differs strongly between the two replicates. The runoff of water volume from one of the dry replicates was even greater than the volume of water running off from both the wet plots.

In combination with the lower glyphosate runoff from the wet plot, this underpins the assumption that higher infiltration of water leads to reduced emission of glyphosate. So, it is assumed that the effect of a higher moisture content of the brick-soil system is overruled by the inherent higher permeability of the wet plot.

A dominating factor determining the infiltration, and thus water runoff, is the permeability of the brick-soil system. The permeability of the pavement itself is mostly not the limiting factor, but the permeability of the soil below (Beltman *et al.*, 2001; p. 36). So, the difference in water runoff between the two plots might be the result of the difference in permeability of the soil layers below the bricks. Then, the permeability of the wet plot is higher than the permeability of the dry plot.

For additional plot experiments, it is of high importance to be able to check the water balance fully. The irrigated volume in the first minutes determines largely the peak concentration in the drained water. Therefore the irrigation rate should be controlled and measured closely.

4.2 Dissipation of glyphosate in time

For the glyphosate extraction experiment on brick, mean recovery was similar for extraction after 3, 72 and 168 hours (approximately 20%). Within the first 3 hours after application, mean recovery can not be differentiated with the data derived from this experiment. After 3 hours the remaining amount of glyphosate (approximately 80%) was dissipated, adsorbed to the brick surface or absorbed by the brick. The actual contribution of adsorption, absorption and photo(transformation) cannot be quantified. Glyphosate present in the bricks after the first wash off is still a potential source of glyphosate runoff. Because the release of glyphosate out of the bricks is driven by molecular diffusion of the glyphosate out of the pore system of the brick, which is a relatively slow process, the concentrations in water running over the surface of the brick will be low compared to the initial peak.

The outdoor experiments did not clarify the effect of the moisture condition of the brick-soil system. which should show the impact the period that a pavement has to dry after the application of the glyphosate. The infiltration capacity of the soil underlying the bricks dominates the observed infiltration process. So, the performed experiments can not underpin the formerly observed effect of the moisture condition of brick-soil system. Beltman *et al.* (2001) observed in one out of four repetitions in an experiment that under wet condition of the brick-soil system the infiltration decreased and therefore the runoff of water and glyphosate increased.

From the experiment with the bricks it was observed that within 7 days the glyphosate mass that could be washed off did not decrease significantly. So, after the application the mass available for washing off on the brick did not decrease. Hence, dissipation of the glyphosate on a dry surface seems to be slow after application.

From the dissipation experiments it is suggested that about 80% of the applied mass remained in the bricks after it had been washed off, so this remaining mass is theoretically to be released (slowly) with next rain showers, assuming that in the time interval between showers the glyphosate in not degraded, because in this period the brick remains dry.

A hard surface may still contain large part of the applied glyphosate. Then it can runoff slowly with water from showers following afterwards. This observation corresponds with monitoring results from Withagen *et al.* (2003) and Zuiderzeeland that after several rain showers still glyphosate is measured in drain and surface waters.

In outdoor situations small rain showers not leading to runoff and the daily temperature cycle leading to morning moist conditions the hard surfaces do not stay dry continuously. Moist conditions in the hard surface may support the degradation of the glyphosate.

5. Conclusions and recommendations

The DOB-recommendation to be evaluated in this study was the advise not to apply glyphosate when rain showers are to be expected in the 48h following the application. This measure has been tested via two research questions: (a) determine the effect of moisture conditions of brick-pavement on runoff of glyphosate to hard surfaces (plot experiment) , and (b) determine the dissipation of glyphosate, applied on bricks from the pavement, in time (dissipation experiment). The setup of the experiments should answer the two questions.

In the plot experiment, a wet pavement did not result in increased runoff of glyphosate in comparison with a dry pavement. In two series, glyphosate runoff was respectively similar and higher from the dry brick pavement than from the wet brick pavement. From the results of the plot experiments it cannot be concluded that a wet brick-soil system gives more runoff than a dry brick-soil system. The difference in infiltration capacity of the soil under the pavement may have caused the difference between the two plots, and not the moisture conditions of the pavement. The infiltration capacity of the soil under the plot that was kept dry, was possibly lower than that of the plot that was wet. So, water starts to flow over the surface of the dry pavement in an earlier stage compared to the wet pavement.

With the dry pavement it was intended to mimic the longer period between the application and the first rain shower; the wet pavement then being the situation with a rain shower shortly after application. Because the plot for the dry situation and the plot for the wet situation differed too much, the effect of the wetness of the hard surface could not be determined.

In the dissipation experiment in which the extraction of glyphosate from bricks was tested showed that after 3 h 24% of the glyphosate mass applied on single bricks exposed to outdoor conditions could be washed off. In the period between 3 h and 168 h after the glyphosate dosed on separate bricks the percentage of the dose that could be washed off did only slightly decrease. Hence, dissipation has not been observed in this period of 165 h. So, some dissipation may have occurred within the first three hours (e.g. volatilisation), but it is most likely that the processes that are responsible for the limited availability of glyphosate after three hours must have been aborption with water into the brick. So the availability for washing off is determined by the extent of penetration into the brick.

After the initial reduction of availability of glyphosate, its availability appears to reduce only slowly in the course of time. Hence, dissipation processes in the time period between the application and the first rain shower hardly reduce the potential runoff of glyphosate on the basis of this test.

Further hard surface characteristics that may affect runoff that can be studied are the impacts of the slope and the infiltration resistance. Research done on infiltration of water in paved systems may contribute to this aspect. Nevertheless, research in infiltration in paved systems is most likely focused on the design of drainage systems in urban areas. Then the focus is on the highest volumes of runoff that may be expected, e.g. intensive and long lasting rain showers. For the purpose of pesticide runoff especially the runoff of water (determined by the infiltration) in the first millimetres of a rain shower determines the pesticide runoff.

In this study it was not extensively determined if dissipation outdoors in uv-light occurred. Therefore further experiments should be done in which the impact of outdoors uv-light on glyphosate on/in hard surface material is determined. The potential of hard surfaces to absorb water and glyphosate depends on the material that the hard surface is made of. Therefore further lab scale experiments should be done to determine the potential of different types of hard surface materials to absorb water and glyphosate.

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Appendix I.
Glyphosate concentrations in aluminium trays

Table 9. Glyphosate concentrations per aluminium tray, translated to kg/ha.

	3 June 2003		17 June 2003	
aluminium tray	dry plot (kg/ha)	wet plot (kg/ha)	dry plot (kg/ha)	wet plot (kg/ha)
1	3.3	2.7	2.6	3.6
2	2.9	2.9	2.5	3.8
3	2.1	2.8	2.5	3.7
4	2.2	3.1	2.2	3.6
5	2.6	2.9	3.6	4.2
mean	**2.6 ± 0.5**	**2.9 ± 0.2**	**2.7 ± 0.6**	**3.8 ± 0.3**

Appendix II.
Collected amount of water in plastic trays

Table 10. Collected amount of water per plastic tray, translated to millimetres on the plot.

	3 June 2003		17 June 2003	
plastic tray	dry plot (mm)	wet plot (mm)	dry plot (mm)	wet plot (mm)
1	7.6	10.9	12.0	19.5
2	19.4	10.7	10.0	13.2
3	14.3	21.0	21.0	21.9
4	16.6	16.9	17.5	16.9
5	15.9	20.6	23.7	12.6
6	14.0	13.7	11.3	16.9
7	8.8	15.4	11.9	29.2
8		11.5	9.1	13.7
mean	**13.8 ±4.2**	**15.1 ± 4.1**	**14.6 ± 5.4**	**18.0 ± 5.6**

Appendix III.
Glyphosate concentrations in runoff water samples

Table 11. Glyphosate concentrations (mg/L) per runoff water sample, on 3 June 2003.

			Dry plot	Wet plot
monster	volume (L)	cumulative volume (L)	glyphosate (mg/ L)	glyphosate (mg/ L)
1	25	25	63.0	45.7
2	25	50	28.3	25.1
3	25	75	18.0	15.8
4	25	100	15.0	11.6
5	50	150	8.7	8.3
6	50	200	5.5	5.4
7	50	250	3.9	4.7
8	50	300	3.2	3.3
9	100	400	2.2	2.5
10	100	500	1.4	1.7
11	100	600	1.2	1.5
12	100	700	0.7	1.3
13	100	800	0.8	1.0

Table 12. Glyphosate concentrations (mg/L) per runoff water sample, on 17 June 2003.

			Dry plot	Wet plot
monster	volume (L)	cumulative volume (L)	glyphosate (mg/ L)	glyphosate (mg/ L)
1	25	25	64.0	36.8
2	25	50	26.8	21.5
3	25	75	15.4	11.7
4	25	100	9.0	8.5
5	50	150	5.6	6.2
6	50	200	4.1	4.1
7	50	250	3.0	3.0
8	50	300	2.2	2.2
9	100	400	1.9	1.8
10	100	500	1.5	1.3
11	100	600	1.0	1.2
12	100	700	0.7	0.8
13	100	800	0.5	0.7

Appendix IV.
Moisture content in soil samples

Table 13. Moisture content (mm) per soil sample before and after irrigation, on 3 June 2003.

	Before irrigation	
	3 June 2003	
under brick	dry plot (mm)	wet plot (mm)
1	9.3	9.2
2	9.6	10.5
3	10.9	12.1
Mean mm	10.0	10.6
Sd	0.8	1.4
	After irrigation	
5	13.8	15.8
6	11.6	15.7
7	13.7	17.0
Mean mm	13.0	16.1
Sd	1.2	0.7

Table 14. Moisture content (mm) per soil sample before and after irrigation, on 17 June 2003.

	Before irrigation	
	17 June 2003	
under brick	dry plot (mm)	wet plot (mm)
1	8.4	9.2
2	8.4	10.1
3	9.6	13.7
Mean mm	8.8	11.0
Sd	0.7	2.3
	After irrigation	
5	13.2	16.4
6	10.7	18.1
7	11.0	23.0
Mean mm	11.6	19.2
Sd	1.4	3.4

Appendix V.

Recovery of glyphosate applied on brick and polyethene foil

Table 15. Recovery of glyphosate applied on brick.

treatment	recovery (%)	mean recovery (%)	standard deviation
control	0	0	
3 hours	27.1		
3 hours	25.4		
3 hours	22.3	24.1	2.2
3 hours	24.0		
3 hours	21.7		
72 hours	22.5		
72 hours	16.3		
72 hours	14.6	16.8	3.6
72 hours	13.0		
72 hours	17.6		
168 hours	28.9		
168 hours	17.7		
168 hours	15.5	18.1	6.5
168 hours	16.8		
168 hours	11.5		

Table 16. Recovery of glyphosate applied on (PE) foil.

treatment	recovery (%)	mean recovery (%)	standard deviation
control	0	0	
4.5 hours	95.6		
4.5 hours	96.2	97.2	2.3
4.5 hours	99.8		
72 hours	57.4		
72 hours	64.7	61.6	3.8
72 hours	62.6		
168 hours	60.6		
168 hours	58.8	61.2	2.7
168 hours	64.2		