PLANT RESEARCH INTERNATIONAL

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WAGENINGEN UR

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Summary

This research was carried out within the project 'Rational Weed Management on hard surfaces' in the period August 2002 until September 2003. This project is sponsored by VEWIN (the Dutch association for drinking water producers), Monsanto Europe (an agrochemical company) and ZHEW (Waterboard Hollandse Eilanden en Waarden).

Herbicide use on public areas has significantly decreased with 68% in the period 1986 – 2001 in the Netherlands. However, a further reduction of the emission of herbicides from hard surfaces to surface waters is desired. Waterboards and drinking water companies in the Netherlands frequently detect herbicides and their metabolites in surface waters. About 75% of the municipalities in the Netherlands use herbicides to control weeds on hard surfaces. Glyphosate, admitted for chemical weed control on hard surfaces in the Netherlands, is the most commonly used herbicide for weed control on hard surfaces.

The aim of this study is to test the effect of a possible emission reducing measure. Two field-scale experiments were carried out under controlled conditions to quantify the effect of applying a buffer-zone (where the herbicide is not applied) around a drain of the sewage system. In one experiment an area of 99 m^2 meter was sprayed with glyphosate while in an other experiment the same area except a 2 meter zone around the drain was sprayed. Emission was expected to be lower when the bufferzone was applied.

In both experiments runoff water and soil samples were collected and analysed on glyphosate and AMPA. Also the moisture content of the soil before and after the experiment was determined.

In experiment 1, in which a 2 meter bufferzone was applied, 19.2% of the applied amount of glyphosate ran off into the drain. In experiment 2, in which no bufferzone was applied, 22.4% emission was determined. The reduction in emission by using the buffer zone was 14.5%. 6.3% Of this reduction is attributed to not spraying in the 2 m bufferzone around the drain and the remaining 8.2% is attributed to infiltration of glyphosate with water during transportation over the surface in the buffer zone.

The results of the field experiments lead to the following conclusions and recommendations:

1. Applying a buffer zone around a drain, in which no glyphosate is applied, reduces runoff of glyphosate to the (rainwater) sewage system.

In practice, weeds are mostly concentrated closely around the drain. As hard surfaces are treated with selective spraying methods, spraying only occurs where weeds are present; not applying herbicides in the buffer zone will reduce runoff more than found in this study in which the whole field was sprayed with glyphosate.

2. Applying glyphosate when the brick/soil system is 'wet' leads to higher runoff rates than from 'dry' brick/soil systems.

Glyphosate present in the bricks after the first runoff is still a potential source of glyphosate runoff, although the concentrations will be low compared to the initial peak runoff.

1. Introduction

Herbicide use in public areas has significantly decreased with 68% in the period 1986 – 2001 in the Netherlands (Loorij, 2003). However, a further reduction of the emission of herbicides from hard surfaces to surface waters is desired. Waterboards and drinking water companies in the Netherlands frequently detect pesticides and their metabolites in surface water.

Glyphosate, admitted for chemical weed control on hard surfaces in the Netherlands, is the most commonly used herbicide for chemical weed control on hard surfaces at present. The legal standard for drinking water is 0.1 μg/L. The Maximum Admissible Risk Level (MAR) in surface waters for glyphosate is 77 μg/L (ad hoc), for AMPA this is 79 μg/L (ad hoc). AMPA is a metabolite of glyphosate (Staats *et al.*, 2002).

About 75% of the municipalities in the Netherlands use herbicides to control weeds on hard surfaces. The main reasons for using chemical weed control are the low costs and the high efficiency. Alternative methods of weed control that do not pollute surface waters, like burning, brushing and hot water treatment, are less effective and more expensive. These methods may also have adverse side effects for the environment like high energy and water use (Saft & Staats, 2002).

This research was carried out to test the effect of a measure to reduce emission of glyphosate from hard surfaces to surface waters. Two field-scale experiments were carried out under controlled conditions to quantify the effect of applying a bufferzone (a zone where herbicides are not applied) around a drain. The drain is the entry to the rainwater sewage system that can transport runoff water to surface waters. By applying a bufferzone a substantial reduction of glyphosate runoff is expected, because this zone contributes relatively most to the runoff. In this zone infiltration occurs minimally because the distance to the drain is short. Infiltration of runoff water and herbicides in brick-pavement is the main process reducing runoff (Beltman *et al.*, 2002, Beltman *et al.*, 2001). In 2003 the effect of weather conditions before and after applying herbicides will be tested. In several experiments the effect of moisture content of the brick-pavement and the soil beneath the pavement on emission will be determined. Complementary, the dissipation of glyphosate on brick-pavement under dry conditions in time will be determined.

In chapter 2 the set-up of the experiments is elaborated. After this the results are presented in chapter 3 and discussed in chapter 4. In chapter 5, the effect of a bufferzone on runoff is analysed in detail. Finally, conclusions and recommendations are given in chapter 6.

2. Material and Methods

Two field-scale experiments were carried out to gain a better insight in the runoff of glyphosate from hard surfaces. In one experiment an area of 99 m^2 meter was sprayed with herbicides while in an other experiment the same area except a 2 meter zone around the drain was sprayed.

In paragraph 2.1 the field experiments are elaborated, in paragraph 2.2 the laboratory analysis of the soil and brick samples is described.

2.1 The field experiments

2.1.1 Description of the experimental field

The experimental field had been used in 2000 for runoff experiments by Beltman *et al.* (2001). The selection of the fields was based on four selection criteria:

1. The hard surface has to be representative for the hard surfaces in the Netherlands where herbicides are applied;
2. Water runoff has to occur, so the surface has to be sloping a little;
3. The field must contain an assembly point for the water running off, for instance a drain;
4. The field has to be large enough so that external influences are negligible.

On the grounds of Plant Research International in Wageningen, a parking place was found that met the criteria. The parking place consisted of brick-pavement. The parking place was constructed in 1972 and was reconstructed in 1999 (to a limited extent replenished with new bricks). The pavement was used regularly by traffic and showed little weed growth. Chemical weed control was not applied to this brick-pavement.

The two experiments were carried out on two separate, comparable experimental fields with a distance between them of approximately 10 meters. The dimensions of the experimental field were 9 m x 11 m (99 m^2). In advance, the experimental field was swept and weeds were removed. The field was staked out with plastic foil filled with sand to make sure that during irrigation, the water deposited outside the experimental field, remained outside the field.

To simulate the precipitation pattern of rainfall as adequate as possible, an irrigation installation that is used in horticulture was used. The installation consisted of 4 PVC-tubes with a length of 10 m each (Plate 1). Each tube had 5 so-called 'Dan sprinklers type 8966' placed on it. These sprinklers deposited maximally 2 L/min and had a maximum spraying diameter of 9 m. The sprinklers were placed on the tube with intervals of 2.5 m. The tubes were placed in the field with a distance between them of 2.5 m. The tubes were positioned approximately 25 cm above the soil surface.

Within the experimental field a drain was present in the middle of the side where the water accumulates (Figure 1). In this drain the runoff was intercepted and pumped by a submerged pump to containers with a volume of 25 L.

Plate 1. Irrigation of the experimental field.

2.1.2 Application of glyphosate

Glyphosate was applied with a portable band spraying device with 6 'Teejet SS 11003' nozzles (Plate 2). The 6 nozzles together had a spraying width of 1.98 m. To prevent differences in doses, the field was sprayed twice with perpendicular walking directions. The experimental field dimensions were 11 m (length) x 9 m (width); the field was sprayed in 5 lanes in length and in 4 lanes in width. To prevent differences in doses and to prevent external influences, 0.75 meter extra was sprayed before and after each spraying lane, outside of the experimental field. These extra meters outside the field were covered with plastic foil (1 m wide). This foil was removed after applying glyphosate. By doing so, contamination of the experimental field later on in the experiment was avoided.

The distribution of the dose on the experimental field was verified by placing aluminium trays on the experimental field before spraying. Concentrations of glyphosate found in these trays varied from 33 mg/L to 44 mg/L in experiment 1 and from 37 mg/L to 54 mg/L in experiment 2. Mean concentration of glyphosate in the aluminium trays in experiment 1 was 0.14 ± 0.02 g/m^2 , in experiment 2 this was 0.15 ± 0.02 g/m^2 (Appendix II). Hence the variation in distribution of glyphosate on the experimental field was less than 15%.

The real dose on the field was calculated out of 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 field. The applied herbicide was Roundup Pro (9.18 ml Roundup pro/L spraying solution), for the applied doses on the experimental fields, see Table 1.

Table 1. Applied dose of glyphosate.

	Experiment 1 on 92.8 m^2 *	Experiment 2 on 99 m^2
dose (g)	18.44	18.48
kg/ha	1.99	1.87

* *bufferzone with radius of 2 m covers 6.2 m^2*

Plate 2. Spraying of glyphosate on the experimental field with bufferzone.

2.1.3 Experimental conditions and sampling

In two field experiments the runoff of glyphosate from brick-pavement was determined. The experiments were carried out on 27 September and 2 October 2002. The day before carrying out the experiment the field was irrigated for 1 hour. This was done to establish an equal starting position of the experiments regarding moisture content of the soil and brick-pavement. No rain fell between irrigation and carrying out the experiments.

In the first experiment, a radius of 2 meter around the drain was covered with plastic foil, before spraying, to prevent this surface from getting sprayed with glyphosate (Plate 2). In the second experiment the entire field surface was sprayed. After spraying, irrigation started when the sprayed surface had become dry (after approximately ¾ - 1 hour). The irrigation intensity was approximately 12 mm per hour (Table 2). Both experiments were carried out until 8 mm (equals 800 L) of water had runoff into the drain and was collected in containers. In previous runoff experiments it was concluded that highest glyphosate concentrations were found in the first 2 mm of runoff water (Beltman *et al.*, 2001). Thereafter, concentrations decreased rapidly. In our experiments irrigation was continued until 8 mm of water had runoff. Most of potential glyphosate runoff should take place within these 8 millimetres.

Table 2. Irrigation in the two experiments.

	Experiment 1	Experiment 2
irrigation intensity (mm/hour)	11.7	12.1
duration of irrigation (min)	69	71

Water running off into the drain was pumped into PVC containers (content 25 L) by a submerged pump (hard polythene and RVS) (Plate 3). 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 this, mixed samples per 100 L runoff water were taken. In total 13 samples were taken (4 of 25 L, 4 of 50 L and 5 of 100 L) per experiment.

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.

Plate 3. Pumping runoff water into PVC containers.

To monitor the distribution of irrigation within the experimental field, 7 pluviometers were placed diagonally across the field (Plate 4 and Appendix I). The collected amount of irrigation in these pluviometers varies from 3.5 mm to 53 mm in experiment 1 and from 3 mm to 29 mm in experiment 2. The mean collected amount of irrigation in the pluviometers in experiment 1 was 17.9 mm ± 16.7, in experiment 2 this was 15.5 mm ± 8.9. Hence, the variation in distribution of irrigation on the experimental field was more than 50%.

Plate 4. Pluviometers placed diagonally across the field.

2.2 Laboratory analysis

In both experiments, runoff water, brick and soil samples were collected. Analysis of brick and soil samples in the laboratory gave information on the amount of herbicide that was absorbed by the brick-pavement and was infiltrated in the ground underneath the surface. The extraction efficiency of brick samples was determined as described in Beltman *et al.* (2001). The extraction efficiency of glyphosate for the brick material was very low (0.7%). Also all the concentrations in the extracts from the bricks were below the detection limit. Therefore it was considered not relevant to further describe and discuss the results.

Before every experiment 4 bricks were removed, in the proximity of the border of the experimental field. Samples of the soil layers underneath these bricks were taken. The soil samples were analysed to describe the starting-point of the experiment. After the experiment 6 bricks in the experimental field were removed and soil samples were taken. Glyphosate was extracted from the soil with water and concentrations were determined. Also the moisture content of the soil taken before and after the experiment was determined.

In addition, the extraction efficiency of glyphosate extracted from soil was determined. After extraction of the soil, all the samples were sent to TNO (Netherlands Organisation for Applied Scientific research) for analysis. The results of the analysis were returned in 2 digits significant.

2.2.1 Soil samples

Before the experiments, four bricks were removed next to the experimental field (Figure 1). Samples of the 0-10 cm and of the 10-20 cm soil layer underneath these bricks were taken (Plate 5). After the experiment 6 bricks in the experimental field were removed and soil samples were taken of the 0–10 cm and 10–20 cm soil layer. Before the experiment, only the samples of soil layer 0-10 cm were analysed. On the parking place where the experimental fields were situated, no chemical weed control was used. No glyphosate was expected to be present in the samples taken before the experiment. The soil samples of both soil layers, taken after the experiment, were analysed. The glyphosate content of the soil samples can be found in Appendix V. To determine the moisture content, samples of both soil layers were taken before and after the experiment. The moisture content of the soil samples can be found in Appendix VI. Time between sampling and extraction of the soil samples was 6 days for experiment 1 and 1 day for experiment 2.

The bulk density of the soil was 1620 kg/m^3. This was calculated from 5 bulk density cores taken of soil layer 0-20 cm in experimental field 1.

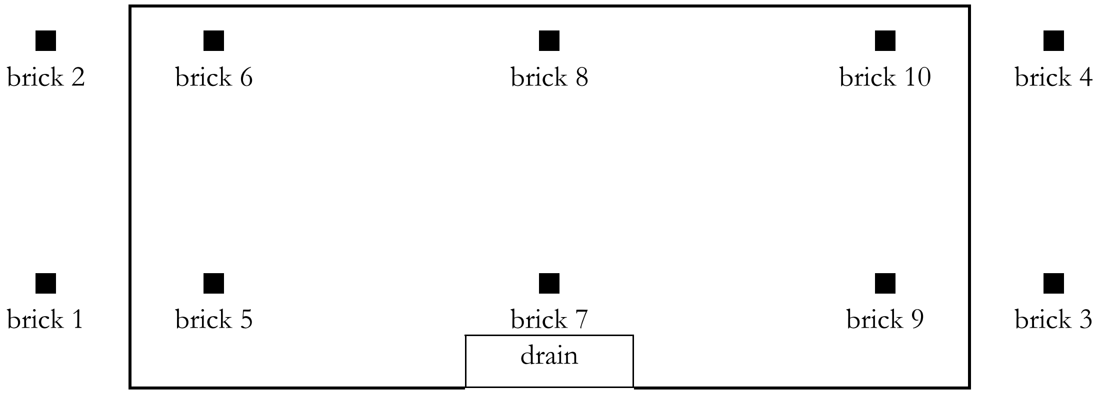

Figure 1. Positions of the bricks below which soil samples are taken.

Plate 5. Taking soil samples before the experiment.

For determining the glyphosate concentration, 100 g of the soil sample was transferred into 200 ml plastic bottles. Added was 100 ml de-ionised water. After this the bottles were shaken for 30 minutes (175 movements/min). The water layer was poured in a test-tube and centrifuged to separate the solid fraction (3000 turns/min) for 10 min. Finally the water layer was poured in PVC sample bottles and all the bottles were send to TNO. The moisture content of the soil was determined by weighing soil in an aluminium cup before and after it was placed in a stove for a night at 105 °C.

2.2.2 Extraction efficiency of soil samples

The extraction efficiency determines the level of representation of the measured glyphosate content of the samples in comparison to the actual content present in soil. To determine the extraction efficiency, soil samples were mixed with a known concentration of Roundup Pro, the formulation of glyphosate also applied in the field experiments.

To determine the extraction efficiency of soil, a mixture of 6 samples of the 0-10 cm soil layer was made of the soil samples collected before the experiment. In 6 plastic bottles (200 ml content) 100 g soil was collected. Added to these samples was 1 ml of solution B (108 ml Roundup Pro/L, equal to 39 mg glyphosate/L). To make sure that soil and solution were properly mixed, the bottle was tilted and while turning the bottle the solution was added. All 6 samples were kept in the fridge at 5 °C. After 1 hour 3 samples (number 1, 2 and 3) were removed from the fridge. Added to the samples was 100 ml de-ionised water and the bottles were shaken for 30 minutes (175 movements/min). After this the water layer was poured in a test-tube and centrifuged to separate the solute fraction. Then the water layer was poured in plastic sample bottles. The sample bottles were placed back in the fridge. The day after, the remaining 3 samples (number 4, 5 and 6) were removed from the fridge and were given the treatment described above. All the sample bottles were sent to TNO for analysis. The mean extraction efficiency of the 6 soil samples was 13.4%. The results can be found in Appendix III.

2.2.3 Analysis of glyphosate and AMPA

Glyphosate and AMPA were analysed by TNO. The substances were measured on a HPCC-system using a fluorescence detector. The samples were derivatised with fluoranylmethyl-chlorformate (FMOC) and pre-concentrated before analysis. The detection limit was 0.5 μg/L for glyphosate and 0.2 μg/L for AMPA.

3. Results

The results of the field experiments include the water balance, the runoff of glyphosate in time and the mass balance of the experiments. Differences in results between experiment 1 and 2 are discussed in chapter 4.

3.1 Water balance

For describing the water balance of the two experiments, determined was:

- The irrigated and collected amount of irrigation (measured);
- The potential absorption of water by the brick-pavement (1,0 mm (Beltman *et al.*, 2001));
- The infiltration of irrigated water in the soil underneath the hard surface (estimated from the increase in moisture content of the soil).

In Table 3 the amount of irrigation on the experimental field and the amount of irrigation that ran off to the drain, is summarised per experiment. In both experiments irrigation was continued until 8 mm (800 L) of water ran off to the drain and was collected in containers. Table 3 shows that in experiment 1 it took 69 minutes to obtain 8 mm of runoff to the drain and in experiment 2 this took 71 minutes. The percentage of irrigated water that ran off to the drain in experiment 1 was 60%, in experiment 2 it was 56%.

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

	Experiment 1	Experiment 2
irrigation intensity (mm/hour)	11.7	12.1
duration of irrigation (min)	69	71
water on experimental field (mm)	13.5	14.3
runoff to drain (mm)	8.0	8.0
runoff to drain (%)	59.5	56.0

The difference between the amount of irrigated water on the experimental field and the amount of water running off, was absorbed by the brick-pavement and infiltrated in the soil below the pavement.

The moisture content of the 0-10 cm soil layer and the 10-20 cm soil layer before and after the experiments was determined (Table 4). Irrigation increased the moisture content of the soil. The moisture content of the soil increased slightly more in experiment 1 than in experiment 2. However, in the second soil layer the moisture content increased more in experiment 2. At the start of the experiments, the moisture content in experiment 2 was lower than the moisture content in experiment 1.

Table 4. Moisture content (percentage on dry matter basis) in soil layers 0–10 cm and 10-20 cm underneath the brick-pavement before and after the experiment.

	Experiment 1		Experiment 2	
Before experiment	Moisture content soil layer 0 –10 cm (%)	Moisture content soil layer 10 –20 cm (%)	Moisture content soil layer 0 –10 cm (%)	Moisture content soil layer 10 –20 cm (%)
Mean	5.5 ± 1.9	8.2 ± 2.4	5.4 ± 1.2	5.4 ± 0.5
after experiment				
Mean	7.4 ± 1.1	9.9 ± 1.8	6.7 ± 1.1	7.4 ± 1.1
Increase in moisture content (%)	1.9	1.7	1.3	2.0
Increase on 99 m^2 (mm)	3.1	2.7	2.1	3.1

In Table 5 the water balance of the experiments is summarised. The uptake of water by the soil was calculated by using the determined bulk density of 1620 kg/m^3. In experiment 1 the amount of irrigation on the experimental field was smaller than in experiment 2. Infiltration in soil however was larger in experiment 1 than in experiment 2. Absorption into the brick-pavement was estimated (Beltman *et al.*, 2001). The water balance is negative in experiment 1 and 0 in experiment 2. It is possible that water has flown to the layer below 20 cm.

Table 5. Water balance of the experiments in mm.

	Experiment 1	Experiment 2
On experimental field (mm)	13.5	14.3
Runoff to drain (mm)	8.0	8.0
Absorption by brick-pavement (mm)	1.0	1.0
Increase in soil layer 0 – 0.20 m (mm)	5.7	5.3
Balance (mm)	-1.2	0.0

Table 6 presents the irrigated millimetres of water derived from the volumes measured with a flow meter in the tube to the sprinklers. This device was read every 15 minutes. The last array in the table gives the amount of millimetres irrigated in the last 9 minutes for experiment 1, and in the last 11 minutes for experiment 2. After this, 8 mm of runoff water was collected and the experiment was stopped. If we translate the amount of irrigated water to 15 minutes the difference between the fifth flux of experiment 1 and 2 is 16.7%. Runoff of irrigation was constant in both experiments. The fluxes were used to determine the amount of irrigation on the experimental fields.

Table 6. Fluxes per experiment in mm per quarter of an hour.

Time (min)	Irrigated in experiment 1 (mm)	Irrigated in experiment 2 (mm)	Differences in irrigation between experiments 1 and 2 in %
0-15	2.88	3.40	17.8
15-30	3.05	2.83	7.3
30-45	2.80	2.75	1.9
45-60	3.06	2.94	4.0
60-end	1.66	2.37	42.7

3.2 Runoff of glyphosate

The runoff of glyphosate was determined on the basis of the concentrations measured in the runoff water (Appendix IV). In figure 2 the concentrations in runoff water are presented as a function of time per experiment. The cumulative runoff is the amount of irrigation that ran off to the drain and was collected in time. The first 2 mm of runoff water contained the highest concentrations of glyphosate in both experiments. Glyphosate concentrations are lower in experiment 1, where the surface in a 2 m radius around the drain was not sprayed, in comparison to experiment 2. In experiment 2 the entire field surface was sprayed.

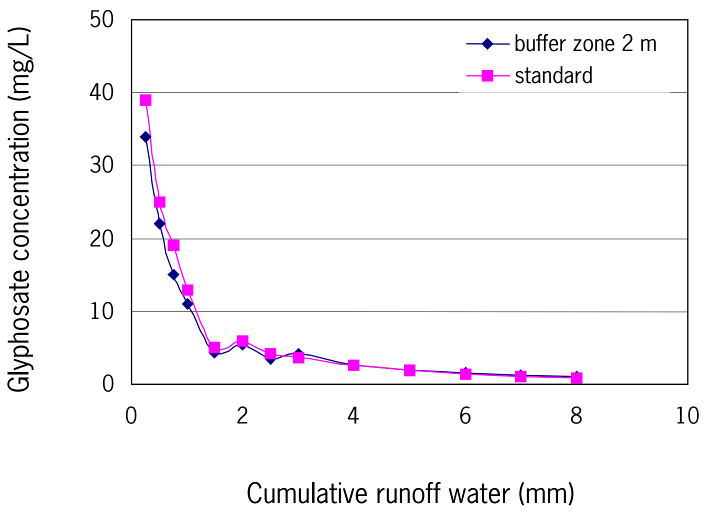

Figure 2. Glyphosate concentration in runoff water in both experiments.

3.3 Mass balance of glyphosate

Before and after carrying out the experiments, samples of the soil were taken. Concentrations of glyphosate present in these samples were determined. With these data the amount of glyphosate infiltration in the 0 till 0.2 m soil layer was determined.

The extraction efficiency of the soil samples was 13.4 %. Because the recovered amounts of glyphosate were constant in all 6 extraction efficiency samples, it can be assumed that the remaining 86.6% was adsorbed to the soil. The total amount of glyphosate was calculated via the assumption that 86.6% in the soil samples was adsorbed to the soil.

The results of the analysis of the soil samples corrected for adsorption are shown in table 7. Before the experiments no samples were taken from the layer 10-20. The table shows that the layer 0-10 did not contain glyphosate above the detection limit, so we assumed that the layer 10-20 was also clean. In both experiments an increase in glyphosate concentrations was found in the first soil layer. The increase was higher in experiment 2 than in experiment 1. The increase of glyphosate mass in the soil layer 0-10 cm underneath the field was calculated with the bulk density of 1620 kg/m^3.

Table 7. Concentrations of glyphosate in soil layer 0-0.1 m and 0.1-0.2 m before (n=4) and after (n=12) irrigation per experiment.

Experiment 1	Before (mg/kg dry soil)	After (mg/kg dry soil)	Increase on 99 m^2 (g)	Increase relative to applied dose (%)
layer 0-0.1 m	<0.0037	0.008 ± 0.01	0.13	0.7
layer 0.1-0.2 m		<0.0037		
Experiment 2				
layer 0-0.1 m	<0.0037	0.10 ± 0.07	1.67	9.0
layer 0.1-0.2 m		<0.0037		

After irrigation, soil samples were taken at 6 points in the experimental field (Figure 1). Because the experimental field was sloping, 3 points were situated higher on the slope than the other 3 points. It can be expected that glyphosate concentrations were higher at the lower situated points than at the higher points, because water runs off to the lowest point, so more water containing glyphosate could infiltrate in the lower part of the field. In Table 8 the glyphosate concentrations in the first soil layer and the increase on the experimental field after irrigation is given for the higher and lower situated part of the fields. The table shows that the increase in glyphosate content of the lower part of the field was about twice the increase in glyphosate content of the higher part of the field.

Table 8. Glyphosate content of soil layer 0-0.1 m after irrigation (n=6) per experiment, split up in the lower part and the higher part of the pavement.

	Low (mg/kg dry soil)	High (mg/kg dry soil)	Low increase on 49.5 m^2 (g)	High increase on 49.5 m^2 (g)
Experiment 1	0.011 ± 0.006	0.006 ± 0.003	0.087	0.045
Experiment 2	0.15 ± 0.061	0.062 ± 0.042	1.19	0.50

In Table 9 the mass balance of glyphosate is given per experiment. In experiment 2 a larger amount of glyphosate ran of to the drain than in experiment 1. In experiment 1 the amount of glyphosate in runoff water was 20.4% of the mass applied on 92.8 m^2, whilst in experiment 2, 22.4% of the mass applied on 99 m^2 ran off. The mass present in the brick pavement after 8 mm water runoff could not be determined. The glyphosate mass in the upper 10 cm of soil underneath the pavement in experiment 2 was approximately 13 times the mass in experiment 1.

Table 9. Mass balance of glyphosate per experiment.

	Experiment 1	Experiment 2
Applied on experimental field (g)	18.4	18.5
in runoff to drain (g)	3.77	4.14
in brick-pavement (g)	Not detected	Not detected
in soil (g)	0.13	1.67
balance (g)	14.5	12.7

4. Discussion

In this chapter first the set-up of the experiment is discussed. Then, the concentration of glyphosate in the soil underneath the pavement and the runoff of glyphosate in the experiments are discussed.

4.1 Set-up of the experiments

In the experiments, we have determined runoff of glyphosate from brick-pavement. In earlier experiments on runoff of glyphosate from asphalt and concrete, it was concluded that mean total loss of glyphosate in 15 mm runoff water was more than twice as high for asphalt (approx. 45%) than for concrete (approx. 20%) (Shepherd and Heather, 1999). This was explained by lower adsorption capacity of asphalt compared to concrete. It was concluded that mass of glyphosate running off depends on the type of hard surface on which it is applied.

Also, the total surface of joints in the hard surface affects runoff of herbicides. When the total joint surface is larger more water can infiltrate into the soil. It is to be expected that with more infiltration of water also a larger amount of herbicide infiltrates into the soil (Beltman *et al.*, 2001).

In the experiments, runoff of glyphosate was determined for a situation where (1) on the entire surface of the experimental field glyphosate was applied except on a radius of 2 m around the drain, and where (2) on the entire surface glyphosate was applied. In practice, only selective methods for applying glyphosate are registered for chemical weed control on hard surfaces. It is assumed that selective spraying results in application of glyphosate on circa 10% of the entire surface. In the experiments the entire surface was sprayed, which is not standard practice, but done to compromise the experimental set-up.

The extraction efficiency of the soil samples was determined in 2 stages. One hour after treatment 3 of the 6 samples were extracted with water. The remaining 3 samples were extracted the day after. The samples that were extracted after 1 hour (number 1, 2 and 3) had higher extraction-efficiencies than the ones extracted after 1 day (Appendix III). It is possible that during the storage in the refrigerator glyphosate had broken down to AMPA or became more strongly adsorbed to the soil (see also 5.2).

4.2 Concentration of glyphosate in soil samples

Increase of concentrations of glyphosate in the soil, corrected for the amount adsorbed to the soil, was smaller in experiment 1 (0.13 g) than in experiment 2 (1.67 g). Time between carrying out experiment 1 and analysing the samples was 6 days, for experiment 2 this was 1 day. The samples were stored in the refrigerator till analysing, at 5 degrees Celsius. The samples taken in experiment 1 have been stored for a longer period in the refrigerator. In this period of time glyphosate could be transformed to AMPA what could explain the smaller increase. However, the degradation DT_{50} at 5 degrees Celsius is 5 days (http://www.ctb-wageningen.nl). The concentrations found in experiment 1 were more than 10 times smaller than concentrations in experiment 2. Transformation of glyphosate to AMPA alone cannot account for the much smaller concentrations in experiment 1 compared to experiment 2. It can be concluded that the increase of glyphosate in the soil in experiment 1 was smaller than in experiment 2.

In the mass balance of glyphosate, 14.5 g was not accounted for in experiment 1, this was 12.7 g in experiment 2. This is probably due to the fact that only very small glyphosate amounts were recovered out of the brick-samples. The increase of glyphosate in the brick-pavement can be underestimated for this reason.

In these experiments no amounts of glyphosate larger than 0.5 μg/L were found in the bricks. The extraction efficiency found for brick-pavement was very low (0.7 %). It is possible that glyphosate was present in the brick-pavement, but the extraction method (shaking brick samples with water) was not adequate enough to remove the glyphosate from the bricks. The crushed brick is possibly a reactive substance that quickly breaks down glyphosate. The amounts of glyphosate present in the bricks can still runoff.

The extraction efficiency for soil was also low (13.36 %). Because the recovered amounts of glyphosate were constant in all 6 extraction efficiency samples, it can be assumed that the remaining 86.64% was adsorbed to the soil. The extraction-efficiencies for soil and brick samples were too low to draw conclusions regarding the exact amount of glyphosate that was absorbed by the brick-pavement and was infiltrated in the ground underneath the surface.

4.3 Runoff of glyphosate

When irrigation starts, a part of the applied glyphosate on top of the hard surface dissolves in the irrigation water and glyphosate infiltrates into the hard surface and the soil. When the soil and the hard surface become saturated (when irrigation intensity is larger than the maximum uptake of soil and brick), runoff of irrigation takes place (Beltman *et al.*, 2001). Assumed is that with higher infiltration of irrigation water in the soil and bricks, more glyphosate enters the soil and the hard surface.

In experiment 1, the increase in moisture content of the first soil layer was 3.1 mm and in experiment 2 the increase was 2.1 mm. The uptake of glyphosate in the soil was proportionally higher in experiment 2 than in experiment 1. This does not agree with the assumption that higher infiltration of irrigation leads to higher glyphosate amounts in the soil. In the first quarter of an hour the water flux in experiment 1 was approximately 18% lower than in experiment 2. Runoff was constant in both experiments. Infiltration in experiment 2 in the first quarter of an hour has to be higher than in experiment 1. This could explain the higher concentrations of glyphosate in the soil in experiment 2.

5. Effect of the bufferzone on runoff

In Figure 3, the total glyphosate mass measured in runoff water relative to the applied amount of glyphosate on 99 m^2 is given for both experiments. In experiment 1, 92.8 m^2 of the surface was sprayed. The amount of applied glyphosate was translated to 99 m^2, so in stead of 18.44 g given in Table 1, an applied mass of 19.7 g was used for calculations. The relative glyphosate runoff was lower in experiment 1 than in experiment 2. In experiment 1, 19.2% of the applied glyphosate mass ran off, in experiment 2 this was 22.4% (Table 10). In former experiments (Beltman *et al.*, 2001), runoff of glyphosate from moist brick-pavement and soil was 23.1%. These results are similar to the results of this experiment.

The reduction in runoff by implementing the buffer zone was 14.5% compared to the situation without bufferzone. 6.3% of this reduction was attributed to not spraying in a radius of 2 m around the drain. The remaining 8.2% was attributed to loss during transport over the surface due to infiltration in the buffer zone.

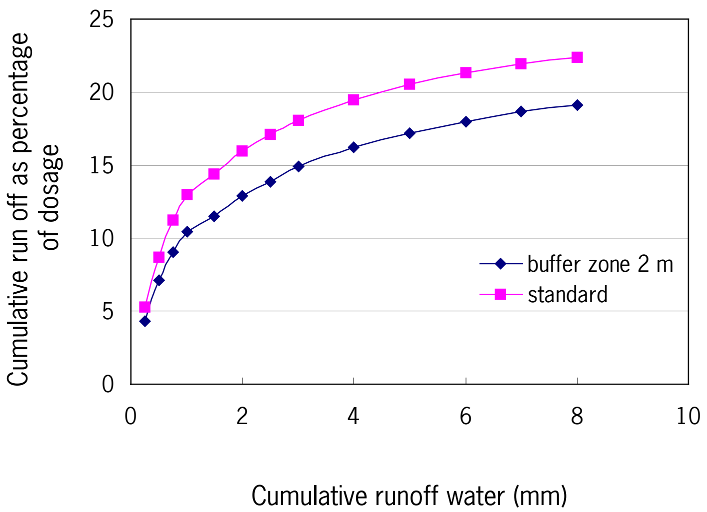

Figure 3. Cumulative glyphosate runoff relative to the glyphosate mass applied on 99 m^2.

The glyphosate mass applied on the experimental field and the total mass in runoff water is summarised in Table 10 per experiment.

Table 10. Glyphosate dose on the experimental fields and total glyphosate masses in runoff water per experiment.

	Experiment 1 on 99 m^2	Experiment 2 on 99 m^2
on experimental field (g)	19.7	18.5
in runoff to drain (g)	3.8	4.1
runoff (%)	19.2	22.4

In practice, weeds would occur mostly around the drains. Due to selective spraying techniques most herbicide would be sprayed on the area directly around the drain. So, when no herbicide is sprayed on the weeds in the buffer zone, the emission reduction effect might be higher than observed in the experiments.

6. Conclusions and recommendations

The aim of the research was to test a measure that could reduce runoff of glyphosate from hard surfaces. The measure tested in this experimental study was the implementation of a bufferzone of 2 m around a drain where no glyphosate was applied. Glyphosate applied within this 2 meter zone was expected to contribute a relatively large part to the total runoff from the paved area. The results of the field experiments lead to the following conclusions:

1. Applying a buffer zone around a drain in which no glyphosate is applied reduces runoff of glyphosate to the (rainwater) sewage system.

In the experiments a reduction of 14.5% of the runoff was found, of which 8.2% was attributed to not spraying the bufferzone, and 6.3% was attributed to the effect of not treating the area from which a relatively large part of the total runoff is expected.

When weeds are mostly concentrated closely around the drain, the buffer zone will reduce the runoff more than found in the experiments in which the whole field was sprayed homogeneously with glyphosate formulation. It is recommended to take into account the distribution of weeds on the hard surface.

2. Applying glyphosate when the brick/soil system is ‘wet’ leads to higher runoff rates than from ‘dry’ systems.

Runoff rates determined in this study corresponded with runoff rates measured in 2000 (Beltman *et al.*, 2001). In the study of Beltman, runoff of ‘dry’ brick/soil systems was about 1/3 of the runoff found in the ‘wet’ system.

3. Glyphosate present in the bricks after the first runoff is still a potential source of glyphosate runoff, although the concentrations will be low compared to the initial peak runoff.

The extraction efficiency for brick samples was too low to draw conclusions regarding exact glyphosate amounts present in the brick-pavement. A recommendation is to use an alternative method for extraction of glyphosate from bricks.

4. Rainfall intensity is supposed to have a major effect on runoff. The large difference between the glyphosate contents in soil combined with higher irrigation intensity in the initial stage in the experiment without bufferzone underpins this.

Weather conditions before and after spraying of herbicides are of key importance for the extent of runoff of the herbicides. For comparing runoff of glyphosate in different experiments, it is wanted that the starting position regarding moisture and glyphosate content of hard surface and soil is similar. This is very difficult to establish because the experiments are performed on different days, where weather conditions of the previous days determine the conditions of the field. Perhaps when experiments are carried out on the same day, the conditions are more similar at and before performing the experiments.

7. References

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Appendix I.

Amount of irrigation water collected per pluviometer

Table 11. Collected amount of irrigation water per pluviometer and per experiment, placed on the experimental field for verifying distribution of irrigation.

Pluviometer	Collected amount of irrigation in experiment 1 (mm)	Collected amount of irrigation in experiment 2 (mm)
1	3.5	3
2	11	21
3	12	19
4	24	29
5	53	14
6	13.5	16.5
7	8	6
mean	**17.9 ± 16.7**	**15.5 ± 8.9**

Appendix II.
Glyphosate concentrations in aluminium trays

Table 12. Concentrations of glyphosate in the aluminium trays per experiment, placed on the experimental field for verifying distribution of the dose.

Aluminium tray	Experiment 1(g/m^2)	Experiment 2 (g/m^2)
1	0.15	0.13
2	0.15	0.14
3	0.11	0.16
4	0.15	0.13
5	0.13	0.19
mean	0.14 ± 0.02	0.15 ± 0.02

Appendix III.
Extraction efficiency of soil samples

Table 13. Extraction efficiency of soil samples. Measured concentration of glyphosate in the solution expressed as percentage of the concentration of the added solution.

Soil sample	Extraction efficiency (%)
1-3	14.9 ± 1.4
4-6	12.1 ± 0.9
overall 1-6	13.4 ± 1.9

Appendix IV.
Glyphosate and AMPA concentrations in runoff water samples

Table 14. Glyphosate and AMPA concentrations (mg/L) in the runoff water samples in experiment 1.

Monster	Volume (L)	Cumulative volume (L)	Glyphosate (mg/ L)	AMPA (mg/L)
1	25	25	34	0.25
2	25	50	22	0.17
3	25	75	15	0.13
4	25	100	11	0.1
5	50	150	4.4	0.068
6	50	200	5.5	0.062
7	50	250	3.5	0.045
8	50	300	4.2	0.05
9	100	400	2.6	0.034
10	100	500	2	0.03
11	100	600	1.5	0.025
12	100	700	1.3	0.021
13	100	800	1	0.017

Table 15. Glyphosate and AMPA concentrations (mg/L) in the runoff water samples in experiment 2.

Monster	Volume (L)	Cumulative volume (L)	Glyphosate (mg/L)	AMPA (mg/l)
14	25	25	39	0.24
15	25	50	25	0.17
16	25	75	19	0.13
17	25	100	13	0.095
18	50	150	5.1	0.066
19	50	200	6	0.057
20	50	250	4.2	0.044
21	50	300	3.6	0.039
22	100	400	2.6	0.029
23	100	500	1.9	0.023
24	100	600	1.4	0.018
25	100	700	1.1	0.015
26	100	800	0.95	0.013

Appendix V.
Glyphosate and AMPA concentrations in soil samples

Table 16. Glyphosate and AMPA concentrations (μg/L) in the soil samples in experiment 1.

Under brick	soil layer 0 – 10 cm. Glyphosate (μg/L)	soil layer 0 – 10 cm. AMPA	soil layer 10 – 20 cm. Glyphosate (μg/L)	soil layer 10 – 20 cm. AMPA
Before irrigation				
1	<0.5	<0.2	n.d.	n.d.
2	<0.5	<0.2	n.d.	n.d.
3	<0.5	1.1	n.d.	n.d.
4	<0.5	2.2	n.d.	n.d.
After irrigation				
5	<0.5	0.2	<0.5	<0.2
6	<0.5	0.5	<0.5	<0.2
7	1.8	4.8	<0.5	3
8	1.1	1.7	<0.5	2.1
9	1.7	2.4	<0.5	0.46
10	<0.5	0.62	<0.5	0.73

N.B. Bricks 6, 8 and 10 are positioned higher on the slope in the experimental field than bricks 5, 7 and 9.

Table 17. Glyphosate and AMPA concentrations (μg/L) in the soil samples in experiment 2.

brick	Soil layer 0 – 10 cm. Glyphosate (μg/L)	Soil layer 0 – 10 cm. AMPA	Soil layer 10 – 20 cm. Glyphosate (μg/L)	Soil layer 10 – 20 cm. AMPA
Before Irrigation				
11	<0.5	<0.2	n.d.	n.d.
12	<0.5	<0.2	n.d.	n.d.
13	<0.5	0.26	n.d.	n.d.
14	<0.5	<0.2	n.d.	n.d.
After Irrigation				
15	17	8.5	<0.5	<0.2
16	8.6	2.9	<0.5	<0.2
17	12	8.5	<0.5	<0.2
18	1.7	0.77	<0.5	<0.2
19	27	13	<0.5	<0.2
20	12	4	<0.5	<0.2

N.B. *Bricks 16, 18 and 20 are positioned higher on the slope in the experimental field than bricks 15, 17 and 19.*
n.d.: *not determined*

Appendix VI.
Moisture content of soil samples

Table 18. Moisture content (%) of the soil samples before and after irrigation, in experiment 1.

	Before irrigation	
Under brick	Soil layer 0-10	Soil layer 10-20
1	4.65	7.34
2	6.18	7.31
3	7.72	11.7
4	3.35	6.42
mean %	**5.48**	**8.19**
sd	1.89	2.38
	After irrigation	
5	5.95	9.38
6	7.79	9.49
7	9.14	8.51
8	6.85	9.02
9	7.96	13.49
10	6.68	9.2
mean %	**7.40**	**9.85**
sd	1.13	1.82

Table 19. Moisture content (%) of the soil samples before and after irrigation, in experiment 2.

	Before irrigation	
under brick	Soil layer 0-10	Soil layer 10-20
11	3.84	5.48
12	6.77	5.06
13	5.7	5.07
14	5.14	6.01
mean %	**5.36**	**5.41**
sd	1.22	0.45
	After irrigation	
15	5.86	6.48
16	6.69	7.00
17	5.74	6.28
18	7.07	7.95
19	6.09	7.11
10	8.69	9.30
mean %	**6.69**	**7.35**
sd	1.10	1.12