



## Short-term transport of glyphosate with erosion in Chinese loess soil – A flume experiment



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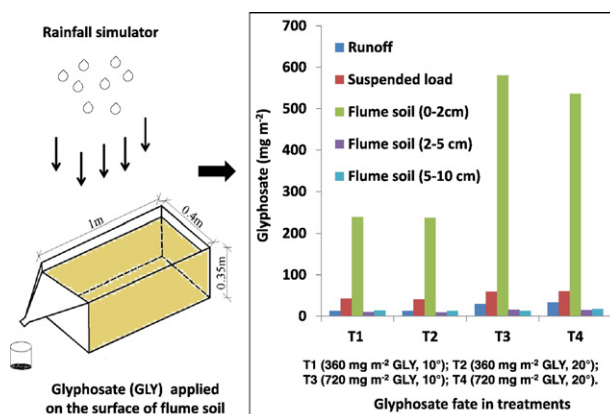
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### HIGHLIGHTS

- Glyphosate transport with erosion in Chinese loess soil was studied.
- Glyphosate and AMPA in runoff and suspended load decreased with rainfall duration.
- Particulate facilitated transport is the main mode for glyphosate transport.
- The risk of glyphosate retained in upper 2 cm soil is higher than in deeper soils.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Repeated applications of glyphosate may contaminate the soil and water and threaten their quality both within the environmental system and beyond it through water erosion related processes and leaching. In this study, we focused on the transport of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) related to soil erosion at two slope gradients (10 and 20°), two rates of pesticide with a formulation of glyphosate (*Roundup*®) application (360 and 720 mg m<sup>-2</sup>), and a rain intensity of 1.0 mm min<sup>-1</sup> for 1 h on bare soil in hydraulic flumes. Runoff and erosion rate were significantly different within slope gradients ( $p < 0.05$ ) while suspended load concentration was relatively constant after 15 min of rainfall. The glyphosate and AMPA concentration in the runoff and suspended load gradually decreased. Significant power and exponent function relationship were observed between rainfall duration and the concentration of glyphosate and AMPA ( $p < 0.01$ ) in runoff and suspended load, respectively. Meanwhile, glyphosate and AMPA content in the eroded material depended more on the initial rate of application than on the slope gradients. The transport rate of glyphosate by runoff and suspended load was approximately 14% of the applied amount, and the chemicals were mainly transported in the suspended load. The glyphosate and AMPA content in the flume soil at the end of the experiment decreased

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significantly with depth ( $p < 0.05$ ), and approximately 72, 2, and 3% of the applied glyphosate (including AMPA) remained in the 0–2, 2–5, and 5–10 cm soil layers, respectively. The risk of contamination in deep soil and the groundwater was thus low, but 5% of the initial application did reach the 2–10 cm soil layer. The risk of contamination of surface water through runoff and sedimentation, however, can be considerable, especially in regions where rain-induced soil erosion is common.

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## 1. Introduction

With the increasing use of agrochemicals, the threat to environments and human health is receiving more attention. Glyphosate (N-(phosphonomethyl)glycine,  $C_3H_8NO_5P$ ), a highly effective broad-spectrum herbicide, is widely used around the world in agriculture, horticulture, parks, and domestic gardens, especially in the cultivation of genetically modified crops (Candela et al., 2007). As a systemic herbicide, glyphosate is intercepted and taken up by the foliage and then enters plant physiological processes that transport it or its principal metabolic product, aminomethylphosphonic acid (AMPA), to the root system, which releases them into the surrounding soils and waters (Laitinen et al., 2007). Applied to bare soil before or after sowing, glyphosate directly reaches the soil and underlies the highest risk of being transported with soil erosion and runoff (Todorovic et al., 2014). The elimination of the glyphosate in the soil mainly depends on microbial degradation through two pathways, one leading to the intermediate formation of sarcosine and glycine, and the other leading to the formation of AMPA (Rueppel et al., 1977). The half-life of a chemical is an important parameter for assessing environmental threats, but estimates of the half-life of glyphosate have ranged from days to months (Al-Rajab and Hakami, 2014; Bergström et al., 2011; Mamy and Barriuso, 2007; Rueppel et al., 1977). The rate of AMPA degradation is also controversial, half-life time ranging from 35 to 151 days (Bergström et al., 2011; Borggaard and Gimsing, 2008; De Jonge et al., 2000). The fate and quantification of glyphosate thus are required to evaluate their threats and to determine the specifics of glyphosate application and related pesticide management (Todorovic et al., 2014; Zablutowicz et al., 2009).

Glyphosate strongly adsorbs on soil particles by ligand exchange through the phosphonic acid moiety (Sheals et al., 2002; Sorensen et al., 2006; Sprankle et al., 1975). Bonded residues of glyphosate are not considered to be bioavailable and therefore not harmful to the environment onsite (Barriuso et al., 2008), but if transported with soil erosion to surface water, the bond residues then enter into the aquatic food chain (Sihtmae et al., 2013). Soil properties and climate also influence the mobility and interactions of glyphosate (Gjettermann et al., 2009; Sorensen et al., 2006; Wang et al., 2005; Zhao et al., 2009; Zhou et al., 2010). Absorbed glyphosate and AMPA can be desorbed at the water–soil interface (Borggaard and Gimsing, 2008; Candela et al., 2007; Coupe et al., 2012; Donald, 2002; Passeport et al., 2014), and competition with phosphates for adsorption sites may lead to free glyphosate rather than the bound form in the soil matrix (Borggaard and Gimsing, 2008; Gimsing et al., 2004; Zhou et al., 2010). The free forms of glyphosate and AMPA are thus easily dispersed, especially in wet soils due to preferential flow (Vereecken, 2005), and heavy rains shortly after glyphosate application increase the entry of glyphosate to surface water bodies through transport with runoff and suspended load (Botta et al., 2009; Candela et al., 2010; Gjettermann et al., 2009; Peruzzo et al., 2008; Stone and Wilson, 2006; Vereecken, 2005).

Luijendijk et al. (2003) reported that up to 24% of the glyphosate sprayed on hard surface soil was transported in runoff to surrounding fields, and Todorovic et al. (2014) showed that approximately 47% of applied glyphosate was transported in the runoff associated with erosion and tillage managements (plough or not). The solubility of glyphosate contributes much to its contamination of surface water, but glyphosate and AMPA bound to particles suspended in water is another means of glyphosate and AMPA transport, known as particle-facilitated

transport (Rügner et al., 2014; VandeVoort et al., 2013). Degenhardt et al. (2012) reported that 67% of added glyphosate was detected in wetland sediment monitoring within 77 days from June to September. Leaching with drainage is another method of glyphosate and AMPA transport that may lead to potential contamination of, and accumulation in, groundwater (Kjær et al., 2011; Ruiz-Toledo et al., 2014; Ulén et al., 2012). Bergström et al. (2011) reported that 0.009 and 0.019% of the glyphosate and AMPA, respectively, were found in leachate samples of a clay soil after 748 days of monitoring in fields. Landry et al. (2005) demonstrated that 0.02–0.06% of applied glyphosate was leached from a calcareous soil column, and Al-Rajab et al. (2008) reported that 0.28, 0.20, and 0.11% of an initial application of  $^{14}C$ -glyphosate were found in leachates of clay loam, silty clay loam, and sandy loam soils, respectively. Leaching occurs after short heavy rains, attributed to an increase in the probability of leaching through soil macropores, especially in unstructured soils (Gjettermann et al., 2009; Kjaer et al., 2005; McGechan, 2002; Stone and Wilson, 2006; Styczen et al., 2011; Vinten et al., 1983). Based on 28 months of field monitoring, 99% of the lost glyphosate ( $5.12 \text{ g ha}^{-1}$ ) was found in the runoff, and glyphosate and AMPA accounted for 0.51 and 0.07%, respectively, of the applied glyphosate (Laitinen et al., 2009). Limited amounts of glyphosate and AMPA are found in leachates and runoff, but the potential risk of contamination in ground/surface water is often not considered, especially by suspended particles (Ruiz-Toledo et al., 2014).

China has become the largest glyphosate supplier in the world, and the thousands of tons of glyphosate-based herbicides are applied to agricultural land each year (Dill, 2005; Zhang et al., 2011). The repetitive use of glyphosate-based herbicides in the field, however, increases the possibility of glyphosate occurrence in, and threat to, soil, plants, surface/ground water (Borggaard and Gimsing, 2008), and animals (Lanctot et al., 2013; Muangphra et al., 2014; Yadav et al., 2013; Zaller et al., 2014). Meanwhile, the risk is particularly high when applied pesticide on bare soil directly before and after sowing. Intensive cultivation with concentrated precipitation releases substantial amounts of agrochemicals, especially on the Loess Plateau in China where soil erosion is common (Shi and Shao, 2000). Nutrients and pesticides in runoff and suspended particles have become the main factors determining water quality, especially in rural regions along rivers (Li et al., 2011). Many studies have focused on glyphosate adsorption, degradation, and leaching in environments, but little is known about glyphosate transport associated with soil erosion (Borggaard and Gimsing, 2008; Donald, 2002). Laitinen et al. (2009) and Todorovic et al. (2014) had experimented (plot observations) under field conditions but only reported glyphosate transport by runoff. Thus, the proposal of the present study was to quantify the transport of glyphosate and AMPA associated with runoff and erosion in Chinese loess soils. The proportion of glyphosate was estimated in runoff, suspended load and soils and the risks for offsite pollution was discussed due to the threats to neighbouring areas of glyphosate application followed directly by rain.

## 2. Materials and methods

### 2.1. Experimental design

#### 2.1.1. Facilities and soils

The experiment was conducted in an artificial rain-simulation facility. Rain intensity was adjusted by nozzle size and water pressure and was calibrated prior to the experiment. The experiment was conducted

in steel hydraulic flumes 1 m long, 0.4 m wide, and 0.35 m deep on a movable platform. The flumes could be adjusted to slope gradients of 0–30°. A V-shaped runoff and suspended load collector was installed at the bottom of each flume to channel the runoff into a collecting receptacle. The soil used in this experiment was a clay loam soil collected from farmland topsoil (0–30 cm) of the Loess Plateau in Yangling, Shaanxi Province, China. Glyphosate has been used for controlling weeds for years and the residues of glyphosate ( $0.01 \mu\text{g g}^{-1}$ ) and AMPA ( $0.01 \mu\text{g g}^{-1}$ ) were detected before we operated the experiment. The soil properties are shown in Table 1.

### 2.1.2. Design

We designed the experiments to test the short-term transport of glyphosate ( $360 \text{ mg m}^{-2}$  and  $720 \text{ mg m}^{-2}$ ) and its main metabolite, AMPA, related to runoff and suspended load. The flumes were inclined at 10° and 20° during 1 h of simulated rain at an intensity of  $1 \text{ mm min}^{-1}$ , representing a typical rain storm in this region of China (Cai et al., 1998). The treatments (T1:  $360 \text{ mg m}^{-2}$ , 10°; T2:  $360 \text{ mg m}^{-2}$ , 20°; T3:  $720 \text{ mg m}^{-2}$ , 10°; T4:  $720 \text{ mg m}^{-2}$ , 20°) were conducted and each treatment was repeated three times.

The soil was air-dried, passed through 5-mm sieves, and mixed thoroughly. We first attached sand (<2 mm) to the flume bottoms to a depth of 5 cm at a density of  $1.35 \text{ g cm}^{-3}$  to prevent the ponding of water and then filled each flume with sieved soil to a depth of 30 cm in six layers of 5 cm each. The surface of each layer was gently raked with a plastic brush before the next layer was packed to minimise the discontinuities between layers. The 0–5 and 5–10 cm layers had bulk densities of  $1.25 \text{ g cm}^{-3}$ , and the lower four layers had bulk densities of  $1.35 \text{ g cm}^{-3}$ , which simulated field conditions monitored when soils were taken. The full-filled flumes were pre-wetted under a  $0.5 \text{ mm min}^{-1}$  rain until runoff was observed at the end of the flume avoiding unevenly roughness of bare soil. Then the flume was covered by plastic canvas and displayed overnight in order to make soil moisture in flume evenly. Then the next day, the flumes were exposed to a  $1 \text{ mm min}^{-1}$  simulated rain storm for 1 h after glyphosate applied. The dynamics of the rain intensity were monitored by six pluviographs around the testing flume during the simulations.

### 2.2. Glyphosate application and sampling

The commercial product Roundup® (Monsanto, produced in Malaysia, Sinochem Agent), glyphosate-based herbicide, containing  $360 \text{ g L}^{-1}$  glyphosate was used for the glyphosate spray solution. The spray solution was prepared by accurately mixing Roundup with deionised water and was stored in plastic containers until use. Flumes were sprayed with 400 mL of prepared glyphosate ( $0.36 \text{ g L}^{-1}$  and  $0.72 \text{ g L}^{-1}$ ) at a nozzle distance of 5 cm above the soil surface of each flume ( $0.4 \text{ m}^{-2}$ ) before being exposed to  $1 \text{ mm min}^{-1}$  rain.

**Table 1**  
Principle properties of selected soil ( $n = 6$ ).

Properties	Value
<i>Particle size distribution:</i>	
<0.002 mm (clay) (%)	$28.5 \pm 0.4$
0.002–0.02 mm (%)	$43.5 \pm 1.3$
>0.02 mm (%)	$28.0 \pm 0.8$
Bulk density ( $\text{g cm}^{-3}$ )	$1.4 \pm 0.1$
pH ( $\text{H}_2\text{O}$ )	$8.1 \pm 0.1$
EC ( $\mu\text{S cm}^{-1}$ )	$146 \pm 1.2$
Cation exchange capacity (CEC) ( $\text{cmol kg}^{-1}$ )	$18.3 \pm 0.6$
Organic matter ( $\text{g kg}^{-1}$ )	$7.6 \pm 0.3$
Total phosphorous ( $\text{g kg}^{-1}$ )	$0.7 \pm 0.01$
Available phosphorous-Olsen ( $\text{mg kg}^{-1}$ )	$17.0 \pm 0.1$
Total Al ( $\text{g kg}^{-1}$ )	$27.5 \pm 0.2$
Total Fe ( $\text{g kg}^{-1}$ )	$32.6 \pm 1.0$
$\text{CaCO}_3$ ( $\text{g kg}^{-1}$ )	$53.7 \pm 0.6$
Total nitrogen ( $\text{g kg}^{-1}$ )	$1.5 \pm 0.1$

Then the rate of glyphosate applied was 360 and  $720 \text{ mg m}^{-2}$  corresponding to 144 and 288 mg glyphosate in each flume. According to the label of Roundup, the pesticide needs to be sprayed again if it rains within 6 h after its application. Based on this, an extreme case was simulated that rain occurs 30 min after glyphosate was applied on the bare soil.

During the rainfall simulation, twenty samples of runoff water and suspended load were collected per flume for each continuously simulated rain at 3-min intervals for 1 h. The runoff with suspended load was volumetrically measured and weighed, and a sample of the supernatant was collected in a 100-mL plastic bottle. The suspended load was allowed to settle and was then separated from the water, dried in a shaded area, and weighed within 48 h. Soil samples were collected at depths of 0–2, 2–5, and 5–10 cm from each flume 20, 50, and 80 cm from the outlet after the simulated 1-h rains for determining the glyphosate and AMPA concentrations. The samples from the same depths in each flume were bulked and then divided into two parts: one for glyphosate determination and the other for immediate soil-moisture analysis. We collected a total of 36 soil samples, 240 water samples, and 240 suspended load samples from four treatments (two application rates and two slope gradients), each with three replicates, for glyphosate detection. All runoff, suspended load, and soil samples were stored at  $-24 \text{ }^\circ\text{C}$  until analysis.

### 2.3. Glyphosate and AMPA determination

#### 2.3.1. Chemicals and solvents

Glyphosate (98%) and AMPA (98.5%) reference standards were obtained from Sigma-Aldrich (USA). Isotopically-labelled glyphosate ( $1, 2\text{-}^{13}\text{C}, ^{15}\text{N}$ ;  $100 \mu\text{g} \cdot \text{mL}^{-1}$ , 1.1 mL) and AMPA ( $^{13}\text{C}, ^{15}\text{N}$ ;  $100 \mu\text{g} \cdot \text{mL}^{-1}$ , 1.1 mL), used as internal standards, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). FMOC-Cl (9-fluorenylmethoxycarbonyl chloride,  $\geq 99.0\%$ ) was purchased from Sigma-Aldrich (Switzerland). Sodium tetraborate decahydrate, a tetraborate buffer ( $\geq 99.5\%$  ACS grade), was purchased from Sigma-Aldrich (USA). Potassium hydroxide (KOH, 85% p.a.) and hydrochloric acid (HCl, 37% ACS, ISO, Reag. Ph Eur grade), were purchased from Merck KGaA (Darmstadt, Germany). Methanol (MeOH, 99.98%) and acetonitrile (99.95%, LC grade) were purchased from Actu-All Chemicals (The Netherlands). Formic acid ( $\geq 98\%$  p.a.) was purchased from Gevaar (The Netherlands). Ammonium acetate ( $\text{NH}_4\text{Ac}$ , approximately 98%) from Sigma (USA) and ammonia solution ( $\text{NH}_3$ , 25%) from Merck KGaA (Darmstadt, Germany) were used for the mobile phases of liquid chromatography–tandem mass spectrometry (LC–MS/MS). Standard stock solutions of glyphosate and AMPA at concentrations of  $2000 \mu\text{g mL}^{-1}$  mixed with the isotope-labelled standards ( $5 \mu\text{g mL}^{-1}$  glyphosate and AMPA) were prepared. KOH (0.6 M) was used for soil extraction, and HCl (6 M) was used to adjust pH before derivatisation. Solutions of 5% borate buffer in Millipore water, 6.5 mM FMOC-Cl in LC-grade acetonitrile, and formic acid (100%) were used for derivatisation. All stock solutions and dilutions were stored at  $4 \text{ }^\circ\text{C}$ .

#### 2.3.2. Extraction and derivatisation

All samples were thawed and homogenised before extraction (soil and suspended load samples) or derivatisation (water samples). For the soil and suspended load samples, 2 g subsamples were transferred to 50 mL plastic centrifuge tubes and were extracted with 10 mL of 0.6 M KOH. The samples were shaken for 1 h in an end-over-end shaker and then centrifuged at 3500 rpm for 30 min. Thereafter, 1 mL of the supernatant was transferred to a plastic tube, and 80  $\mu\text{L}$  of 6 M HCl was added to adjust the pH to approximately 9 before derivatisation. For the water samples, 1 mL of the sample was directly transferred to a plastic tube and immediately derivatised.

The derivatisation step was the same for all samples. Forty microlitres of the  $5 \mu\text{g mL}^{-1}$  isotope-labelled standard glyphosate and AMPA solution were added to each soil/suspended load extract

or water sample, and 0.5 mL of 5% borate buffer and 0.5 mL of FMOC-Cl were then added. The tubes were shaken manually and incubated for 30 min at room temperature. The reaction was stopped by adding 50  $\mu\text{L}$  of concentrated formic acid. All samples were then shaken manually, and 0.5 mL was transferred to plastic LC vials integrated with 0.45- $\mu\text{m}$  PFTE filters. All samples were prepared in duplicate. The solvent standards were derivatised with the samples for each batch of samples.

### 2.3.3. LC-MS/MS

Glyphosate and AMPA concentrations were determined by LC-MS/MS using an XBridge™ Shield RP C18 column (3.5- $\mu\text{m}$  particle size, 150 mm in length, 2.1-mm i.d.) (Waters, The Netherlands). The mobile phases consisted of 5 mM  $\text{NH}_4\text{Ac}$  in Millipore water (solvent A, pH = 9) and a 9:1 MeOH:H<sub>2</sub>O (Millipore) solution (solvent B, pH = 9). The pH was adjusted to approximately 9 using 25%  $\text{NH}_3$ . The LC-gradient times for the separation were: isocratic from 0 to 1 min (100% A:0% B); from 1 to 6 min, a linear increase of B from 0 to 100%; isocratic from 6 to 8 min (0% A:100% B); from 8 to 9 min, a linear decrease of B from 100 to 0%; and isocratic from 9 to 14 min (100% A:0% B). Initial conditions were re-established in 1 min for a total run time of 15 min. The column temperature was 35.0 °C, and the flow rate was 0.4 mL  $\text{min}^{-1}$ . Optimisation of the ionisation and fragmentation conditions for the analytes was obtained by the infusion of solutions of the individual FMOC analytes. Optimum responses were obtained by electrospray ionisation in negative-ion mode using the following source parameters: capillary voltage of 3.5 kV, cone voltage of 20 V, source temperature of 120 °C, desolvation gas temperature of 400 °C, and gas flows of 160–200 L  $\text{h}^{-1}$  (cone) and 580–600 L  $\text{h}^{-1}$  (desolvation). The transitions acquired for the FMOC derivatives of glyphosate, AMPA, and their corresponding labels are given in Table 2.

### 2.3.4. Quality control

The quantification of glyphosate and AMPA in the samples was based on multi-level calibrations using solvent standards containing the isotopically labelled internal standards. The responses of glyphosate and AMPA were normalised to those of the corresponding internal standards, thereby correcting for any effects of ion suppression (or enhancement) in the LC-MS/MS measurements. Standard calibration curves at concentrations of 0, 0.02, 0.04, 0.1, 0.2, 0.4, 1.0, and 2.0  $\mu\text{g mL}^{-1}$  indicated satisfactory linearity, with correlation coefficients >0.99 and residuals lower than  $\pm 20\%$  response. The method was validated in two matrices: soil and water. The soil used for the validation was from the Loess Plateau, and the water samples were the tap water used for the rain simulations. Soil samples were spiked and analysed in quintuplicate at concentrations of 0.05, 0.1, 0.2, 0.5, and 1  $\mu\text{g g}^{-1}$ . Spiked water samples were analysed in quintuplicate at concentrations of 0.01 and 0.5  $\mu\text{g mL}^{-1}$ . Unspiked soil and water samples were also analysed to confirm the absence of glyphosate and AMPA residues in the blank samples. The recoveries and replicabilities of the analysis of the spiked samples are presented in Table 3. The limits of quantification (LOQ), defined as the lowest concentration tested for

**Table 2**

Transitions measured for the FMOC-derivatives of glyphosate, AMPA and their isotopically-labelled internal standards.

Analyte	Precursor ion (m/z)	Product ion (m/z)	Dwell (sec)	Collision energy (eV)
AMPA-FMOC	332.20	Q: 110.20	0.05	6.00
AMPA-FMOC	332.20	q: 136.10	0.05	14.00
<sup>13</sup> C <sup>15</sup> N AMPA-FMOC	334.20	Q: 112.20	0.05	6.00
Glyphosate-FMOC	390.20	q: 124.20	0.05	28.00
Glyphosate-FMOC	390.20	q: 150.20	0.05	24.00
Glyphosate-FMOC	390.20	Q: 168.10	0.05	12.00
1,2- <sup>13</sup> C <sub>2</sub> <sup>15</sup> N glyphosate-FMOC	390.20	Q: 171.10	0.05	12.00

Q: Transition used for quantification; q: transition used for confirmation.

**Table 3**

Summary of validation data.

Chemical	LOQ (LOD)		Average recovery (%) and SD	
	Soil ( $\mu\text{g g}^{-1}$ )	Tap water ( $\mu\text{g mL}^{-1}$ )	Soil	Tap water
	(n = 25)	(n = 10)	(n = 25)	(n = 10)
Glyphosate	0.05 (0.030)	0.01 (0.0064)	77 $\pm$ 6	78 $\pm$ 5
AMPA	0.05 (0.039)	0.01 (0.0073)	81 $\pm$ 6	76 $\pm$ 6

which an average recovery between 70–120% and a relative standard deviation  $\leq 20\%$  are obtained, were 0.05  $\mu\text{g g}^{-1}$  for soil and 0.01  $\mu\text{g mL}^{-1}$  for water, for both glyphosate and AMPA. The limits of detection (LOD) (S:N = 3) were 0.030  $\mu\text{g g}^{-1}$  for glyphosate and 0.039  $\mu\text{g g}^{-1}$  for AMPA in soil and 0.0067 and 0.0074  $\mu\text{g mL}^{-1}$  for glyphosate and AMPA in tap water. The analytical results for the soil, suspended load, and water samples were corrected for the recovery using standard calibrations at concentrations of 0.2  $\mu\text{g mL}^{-1}$ .

### 2.4. Data analysis

The data were summarised by calculating the mean and standard deviation of the replicates. The runoff and erosion rates were calculated based on runoff volume, dried suspended load weight, sampling time, and flume area:

$$R = \frac{V}{A \times t} \quad (1)$$

$$E = \frac{m_{\text{sus}}}{A \times t} \quad (2)$$

where  $R$  is the runoff rate,  $\text{mL m}^{-2} \text{min}^{-1}$ ;  $V$  is the volume of the runoff, mL;  $t$  is the sampling time, min;  $E$  is the erosion rate,  $\text{g m}^{-2} \text{min}^{-1}$ ;  $m_{\text{sus}}$  is the dry weight of the suspended load, g; and  $A$  is the surface area of the flume,  $\text{m}^2$ .

The amount of transport of glyphosate and AMPA for different simulation times was calculated by:

$$m_{\text{Tg}} = \frac{\sum_i^n (V \times C_{\text{rg}}) + \sum_i^n (m_{\text{sus}} \times C_{\text{susg}})}{1000 \times A} \quad (3)$$

$$m_{\text{Ta}} = \frac{\sum_i^n (V \times C_{\text{ra}}) + \sum_i^n (m_{\text{sus}} \times C_{\text{susa}})}{1000 \times A} \quad (4)$$

where  $m_{\text{Tg}}$  is the amount of glyphosate transported by the runoff and suspended load,  $\text{mg m}^{-2}$ ;  $m_{\text{Ta}}$  is the amount of AMPA transported by the runoff and suspended load,  $\text{mg m}^{-2}$ ;  $C_{\text{rg}}$  is the glyphosate content of the runoff,  $\mu\text{g mL}^{-1}$ ;  $C_{\text{susg}}$  is the glyphosate content of the suspended load,  $\mu\text{g g}^{-1}$ ;  $C_{\text{ra}}$  is the AMPA content of the runoff,  $\mu\text{g mL}^{-1}$ ;  $C_{\text{susa}}$  is the AMPA content of the suspended load,  $\mu\text{g g}^{-1}$ ;  $i$  is the  $i$ th sampling time, min; and  $n$  is the total simulation time. The residual glyphosate and AMPA in the soil was calculated by:

$$m_{\text{sg}} = \frac{\sum_j^k (m_{\text{sj}} \times C_{\text{sgj}})}{1000 \times A} \quad (5)$$

$$m_{\text{sa}} = \frac{\sum_j^k (m_{\text{sj}} \times C_{\text{sa}j})}{1000 \times A} \quad (6)$$

where  $m_{\text{sg}}$  is the total amount of glyphosate in the soil,  $\text{mg m}^{-2}$ ;  $m_{\text{sa}}$  is the total amount of AMPA in the soil,  $\text{mg m}^{-2}$ ;  $m_{\text{sj}}$  is the soil weight in the  $j$ th soil layer, g;  $C_{\text{sgj}}$  is the glyphosate content of the  $j$ th soil layer,  $\mu\text{g g}^{-1}$ ;  $C_{\text{sa}j}$  is the AMPA content of the  $j$ th soil layer,  $\mu\text{g g}^{-1}$ ;  $j$  is the depth of the soil layer in the flume, cm; and  $k$  is the total number of sampled soil layers.

In addition, in order to trace glyphosate in this study, AMPA was calculated as a glyphosate equivalent using molecular mass (transfer coefficient of 1.52). Due to the limit of the residual of glyphosate and AMPA in soil before experiment conducted, the glyphosate recovery was then determined by:

$$R_d = \frac{m_{Tg} + m_{sg} + 1.52 \times (m_{Ta} + m_{sa})}{m} \times 100\% \quad (7)$$

where  $R_d$  is the recovery of glyphosate, %; and  $m$  is the applied glyphosate in each flume,  $\text{mg m}^{-2}$ .

The statistical analysis was performed using SPSS 20.0 and graphs were made by SigmaPlot 10.0. The data in the figures represent the means of triplicate samples. Data distributions were tested for normality with Kolmogorov–Smirnov tests. The significance of differences between the treatments at each time step ( $p < 0.05$ ) was determined by analyses of variance followed by Dunnett's T3 tests. Regression analysis estimated the dynamic fitted curve between the concentration of glyphosate and AMPA in runoff and suspended load and rainfall duration.

### 3. Results

#### 3.1. Runoff rate, erosion rate and suspended load concentration

Temporal variation of the runoff rate, erosion rate and suspended load concentration in different treatments illustrated that the runoff rate and erosion rate were significantly higher in T2 and T4 than in T1 and T3 but not the suspended load concentration (Fig. 1a–c). In the  $10^\circ$  slope treatments (T1, T3), runoff rate increased in the first 15 min and then reached a steady-state at  $0.64 \pm 0.01 \text{ L m}^{-2} \text{ min}^{-1}$ . In the  $20^\circ$  slope treatments (T2, T4), runoff rate increased in the first 21 min then steadied at  $0.82 \pm 0.01 \text{ L m}^{-2} \text{ min}^{-1}$  (Fig. 1a). Erosion rate increased in the first 15 min in T1 and T3 but then decreased to a rate of  $13.18 \pm 0.71 \text{ g m}^{-2} \text{ min}^{-1}$  in T1 and  $11.06 \pm 1.97 \text{ g m}^{-2} \text{ min}^{-1}$  in T3. The erosion rate in T2 and T4, however, peaked in the first 9 min at  $23.11 \text{ g m}^{-2} \text{ min}^{-1}$  and then declined gradually to steady states of  $18.86 \pm 2.49$  and  $17.16 \pm 1.17 \text{ g m}^{-2} \text{ min}^{-1}$  in T2 and T4, respectively (Fig. 1b). Suspended load concentration differed significantly in the first 9 min of  $10^\circ$  and  $20^\circ$  slope treatments ( $p < 0.05$ ) and then levelled  $0.0175 \pm 0.01$  and  $0.0196 \pm 0.02 \text{ kg L}^{-1}$ , in  $10^\circ$  (T1 and T3) and  $20^\circ$  (T2 and T4) (Fig. 1c). Therefore, runoff and erosion rate were significantly different between the two slope gradients ( $p < 0.05$ ) while suspended load concentration was relatively constant (Fig. 1a–c).

#### 3.2. The distribution of glyphosate and AMPA in the runoff and suspended load

##### 3.2.1. Glyphosate and AMPA concentrations in the runoff

The concentration of glyphosate in the runoff differed significantly between the treatments (T1/T2 and T3/T4) ( $p < 0.01$ ) at the beginning of the first 15 min rainfall for the two initial glyphosate application rates (Fig. 2a). The maximum of glyphosate concentration was detected in the first 3 min, 1.64 and  $1.12 \mu\text{g mL}^{-1}$  in T1 and T2 and 2.90 and  $2.75 \mu\text{g mL}^{-1}$  in T3 and T4, respectively. Then the rapid decrease in concentration was followed by a slower decrease, reaching a steady state at  $0.10 \pm 0.02 \mu\text{g mL}^{-1}$  in T1/T2 and  $0.17 \pm 0.03 \mu\text{g mL}^{-1}$  in T3/T4 after 42 min of rain. Similarly, the AMPA concentrations in the runoff peaked at 0.03 and  $0.02 \mu\text{g mL}^{-1}$  in T1 and T2 and 0.08 and  $0.04 \mu\text{g mL}^{-1}$  in T3 and T4, respectively, in the first 3 min and then decreased considerably to steady states of  $0.013$  and  $0.004 \mu\text{g mL}^{-1}$  in T3/T4 and T1/T2, respectively, after 42 min (Fig. 2b). It is clear that the AMPA concentration in T3 and T4, treated with a higher amount of glyphosate, however, was significantly higher than those in T1 and T2 ( $p < 0.01$ ). The concentrations of glyphosate and AMPA decreased during the simulated rain and could be described by significant power functions ( $p < 0.01$ ) (Fig. 2 a–b).

##### 3.2.2. Glyphosate and AMPA content in the suspended load

The glyphosate and AMPA content in the suspended load, similar to the concentration in the runoff, decreased during the simulation time (Fig. 3a–b). The glyphosate content was slightly higher (but not significantly) for the lower slope gradient ( $10^\circ$ ) than for the higher gradient ( $20^\circ$ ) in the treatments with the same rate of application. Glyphosate content decreased rapidly in the first 15 min of simulated rain in all treatments, from  $84.87 \pm 2.99$  to  $24.05 \pm 4.97 \mu\text{g g}^{-1}$  in T1 and T2 and from  $113.11 \pm 11.05$  to  $42.57 \pm 2.88 \mu\text{g g}^{-1}$  in T3 and T4, respectively. Thereafter, the glyphosate content decreased more gradually, reaching relatively steady levels of  $17.98 \pm 2.36$  in T1/T2 being significant lower than  $32.92 \pm 2.98$  in T3/T4 (Fig. 3a). The AMPA content, however, was higher for the  $20^\circ$  slope than for the lower slope at the same application rate. The significant differences of AMPA content in suspended load between T1 and T2/T3/T4 were observed at the first 15 min and then decreased without significant differences in treatments ( $p < 0.05$ ) (Fig. 3b). According to the content of glyphosate and AMPA in the suspended load, a strong significant exponent relationship was estimated with rain duration (Fig. 3a–b).

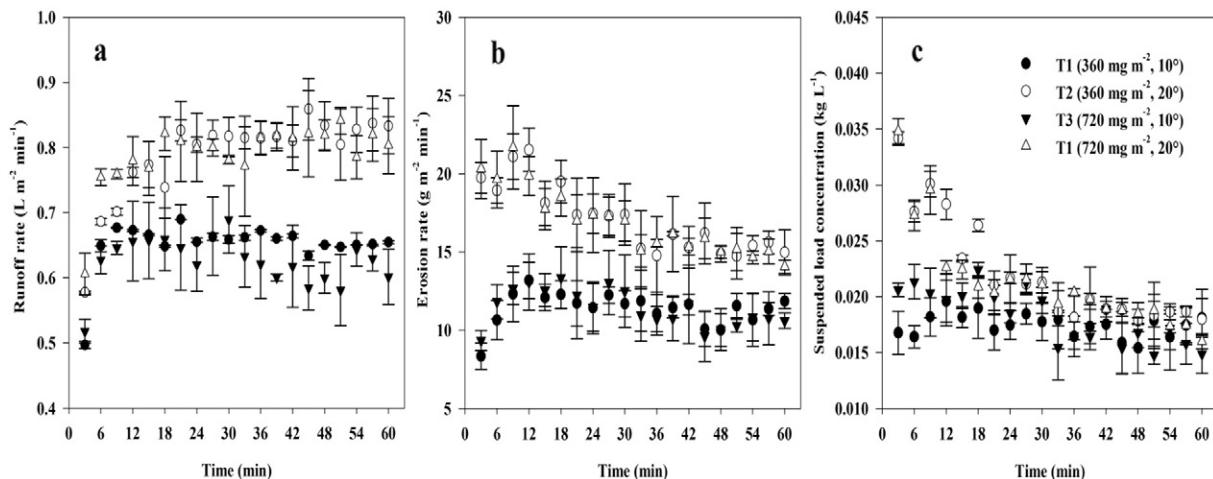


Fig. 1. Temporal variation in the Runoff rate, erosion rate and suspended load concentration in different treatments: (a) runoff rate, (b) erosion rate, (c) suspended load concentration.

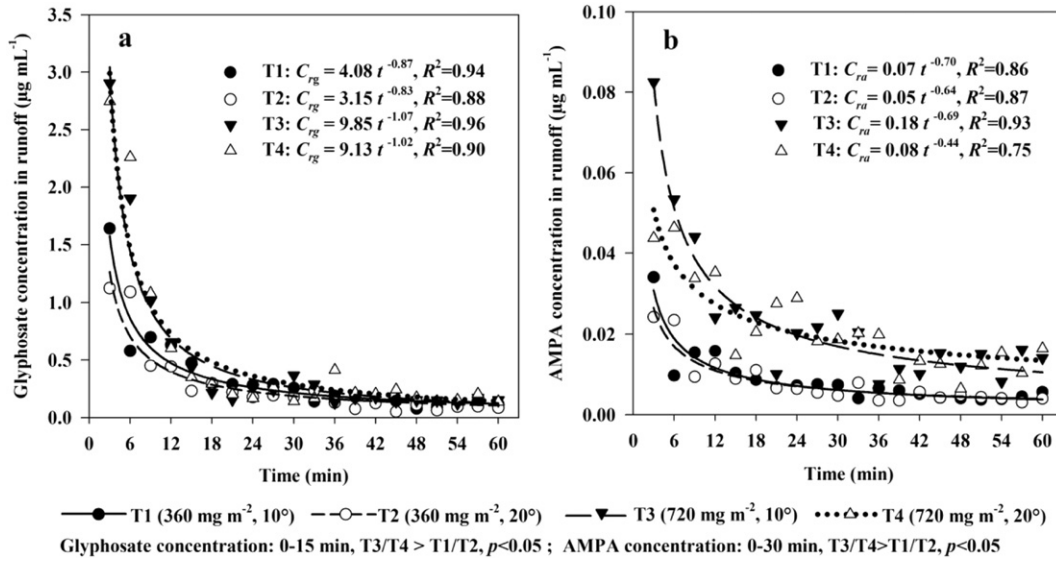


Fig. 2. Glyphosate and AMPA concentration in runoff of different treatments: (a) glyphosate concentration in runoff (T3/T4 > T1/T2,  $p < 0.05$ , 0–15 min), (b) AMPA concentration in runoff (T3/T4 > T1/T2,  $p < 0.05$ , 0–30 min).

### 3.3. The residual glyphosate and AMPA in the flume soil

The residual glyphosate content in the flume soil was detected mainly in the top 2 cm and decreased significantly with depth ( $p < 0.05$ ) (Table 4). The glyphosate content in the surface soil differed significantly in treatments, with 8.12/8.28 and 21.29/18.91  $\mu\text{g g}^{-1}$  in T1/T2 and T3/T4, respectively. Glyphosate was detected at depths of 2–5 and 5–10 cm, but the contents in three of the samples were near the limit of detection. AMPA, however, was detected in the deeper soil layers of the treatments, and the content decreased with soil depth, except in the 5–10 cm layer. AMPA contents in the top soil (0–2 cm) also differed significantly between T1/T2 and T3/T4.

### 3.4. Glyphosate fate in the short-term rainfall

The distribution of glyphosate and AMPA was monitored and the significant differences were observed in the runoff, suspended load, and different soil layers ( $p < 0.05$ ) (Fig. 4). The transport of glyphosate

in the runoff (4%) and suspended load (10%) was limited compared to the residual contents in the top soil (0–2 cm) which represented 72% of the initial application amount in the treatments. The accumulated transport of glyphosate (including AMPA) was summed for different rainfall durations (Table 5). Nearly half of the transported glyphosate was transported within the first 15 min, and the transport rate then gradually decreased. Interestingly, the initial application rate in T3 and T4 was doubled in T1 and T2, but the rate of transport in the runoff and suspended load was similar to that in T1 and T2, with  $14 \pm 1\%$  of the transport rate of glyphosate within 1 h erosion rainfall. The residual glyphosate (including AMPA) in the flume soil apparently depended on the initial application rate. The total amounts of glyphosate and AMPA in the deeper soil layers were very limited, only 2 and 3% in the 2–5 and 5–10 cm layers, respectively. In total,  $76 \pm 6\%$  of the applied glyphosate was detected in runoff, suspended load and soil after an hour of rainfall and the recovery of glyphosate was as high as  $91 \pm 4\%$  calculating AMPA as parent glyphosate (mass balance).

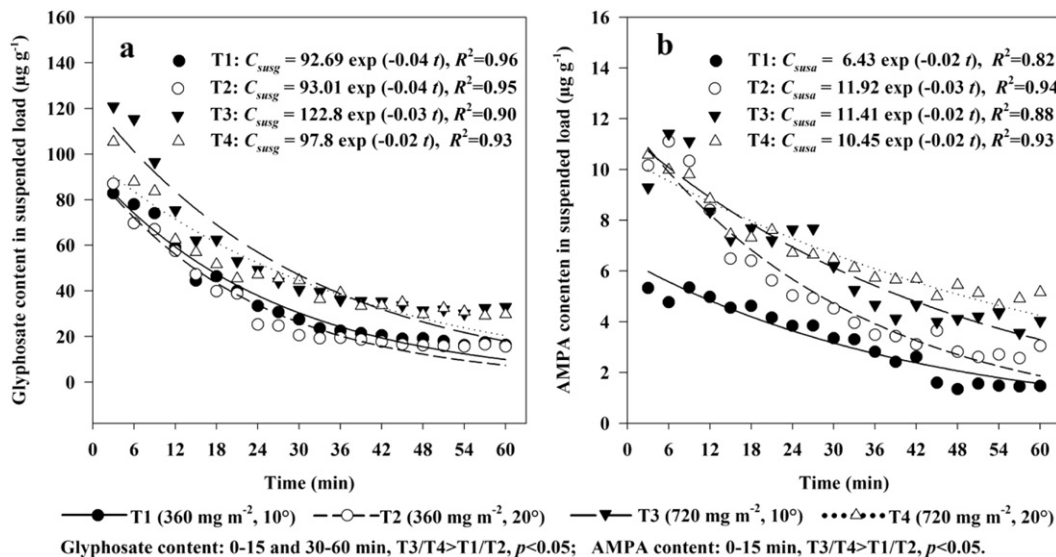


Fig. 3. Glyphosate and AMPA content in suspended load in different treatments: (a) glyphosate content in suspended load, (b) AMPA content in suspended load.

**Table 4**  
Glyphosate and AMPA content in different soil depth of treatment ( $n = 3$ ).

Treatment	Depth (cm)	Glyphosate content ( $\mu\text{g g}^{-1}$ )	AMPA content ( $\mu\text{g g}^{-1}$ )
T1	0–2	$8.12 \pm 0.67\text{a}$	$0.70 \pm 0.09\text{a}$
	2–5	$0.03 \pm 0.01\text{b}^*$	$0.16 \pm 0.02\text{b}$
	5–10	$0.02 \pm 0.00\text{b}^*$	$0.12 \pm 0.01\text{b}$
T2	0–2	$8.28 \pm 0.10\text{a}$	$0.88 \pm 0.09\text{a}$
	2–5	$0.04 \pm 0.00\text{b}^*$	$0.14 \pm 0.00\text{b}$
	5–10	$0.04 \pm 0.01\text{b}^*$	$0.11 \pm 0.01\text{b}$
T3	0–2	$21.29 \pm 0.73\text{a}$	$1.27 \pm 0.17\text{a}$
	2–5	$0.03 \pm 0.01\text{b}^*$	$0.25 \pm 0.02\text{b}^*$
	5–10	$0.02 \pm 0.00\text{b}^*$	$0.12 \pm 0.01\text{b}^*$
T4	0–2	$18.91 \pm 0.56\text{a}$	$1.65 \pm 0.03\text{a}$
	2–5	$0.02 \pm 0.00\text{b}^*$	$0.24 \pm 0.01\text{b}^*$
	5–10	$0.03 \pm 0.01\text{b}^*$	$0.16 \pm 0.01\text{b}^*$

The content of glyphosate and AMPA is given as means  $\pm$  standard deviations. The means followed by the same letter do not differ at the 95% confidence level.

\* Glyphosate and AMPA were detected but the content was below LOQ.

#### 4. Discussion

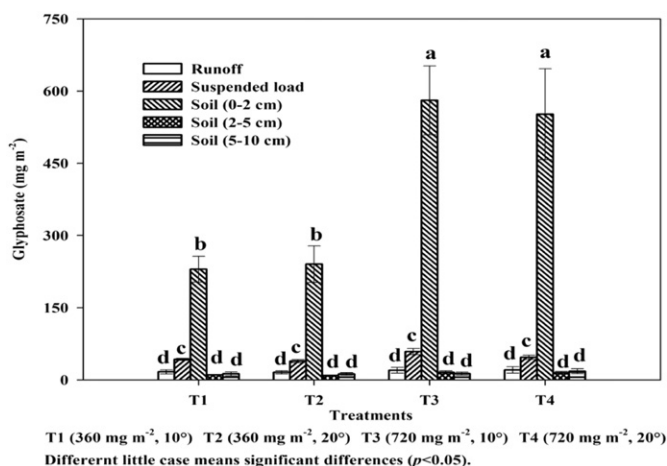
With the increased use of glyphosate-based herbicides, the occurrence of glyphosate and its metabolite AMPA derived from intensive agriculture triggers great attention being paid on the risks of glyphosate in environment (Qiu et al., 2013; Zaller et al., 2014). In highly erodible land, together with runoff and suspended load, glyphosate and AMPA, supposedly, are transported, deposited, and probably accumulated in nearby areas (Ulén et al., 2014). However, the occurrence of glyphosate cannot be explained by agricultural use only attributing to the comparison of agricultural application and the seasonal concentration and load pattern (Botta et al., 2009; Hanke et al., 2010; Huang et al., 2004; Kolpin et al., 2006). The freely glyphosate and AMPA from farmland or urban sewer are dissolved in runoff/water involving dilution, dissipation and degradation in the receiving water system (Harmon, 2008; Majewski et al., 2014). The risk of offsite transport glyphosate and AMPA should be particularly evaluated due to the heavy rain after glyphosate-based herbicides application (Hanke et al., 2010; Styczen et al., 2011). Admittedly, with the duration of rainfall and the distance of transport route, the dilution effect on pollutant has been considered a solution to reduce the risk based on the environmental load but it is also debated (Floehr et al., 2013). EPA (2003) reported that  $1.1 \mu\text{g L}^{-1}$  of glyphosate was detected which is ten times of the EU limit value ( $0.1 \mu\text{g L}^{-1}$ ) for this herbicide in groundwater while the level of glyphosate/AMPA in public water system is seldom reported comparing to the studies of them in

soils, China (Zhao et al., 2009; Zhou et al., 2010). Although precipitation dilutes the concentration of pollutants, the level of glyphosate and AMPA in the runoff of this study was still high which is in accordance with other studies (Ramwell et al., 2014; Ruiz-Toledo et al., 2014; Todorovic et al., 2014). Concerning the exceeding load of glyphosate and AMPA in water, the potential threat to aquatic ecosystem has been reported (Muangphra et al., 2014; Yadav et al., 2013; Zhou et al., 2013). Thus, glyphosate-based herbicide application needs to be controlled especially in the region with much precipitation and water erosion (Majewski et al., 2014; Ramwell et al., 2014).

Raindrop-induced soil erosion increases the mobility of chemicals which are combined with soil particles transporting together with overland flow (Stone and Wilson, 2006; Todorovic et al., 2014). The fact is that glyphosate and AMPA are strongly absorbed in soil particles after sprayed on the surface of soil, regardless of dissolution ( $0.01 \text{ g mL}^{-1}$ ,  $20^\circ\text{C}$ ) and desorption in soil matrix (Gimsing et al., 2004). Once soil erosion occurs, the bound glyphosate and AMPA can be detached and washed together with soil particles (Degehardt et al., 2012; Todorovic et al., 2014). Regarding the carrier of glyphosate and AMPA, in this study, the main transport mode for glyphosate and AMPA is particle-facilitated transport which is in agreement with the results of Degehardt et al. (2012). However, in the past, most of the models have been developed to assess the risks of dissolution pollutants, such as nitrogen, phosphorus, and even pesticides in environmental system while the models to assess the potential risk of chemicals transported by particle-facilitated mode are rare (Schulz, 2004). Therefore, the gap in this field needs to be concerned due to glyphosate properties and its intensive use (Zhang et al., 2011).

The chemicals transported via soil macropores during intensive rain may enhance the movement of substances (Jarvis, 2007; Lowry et al., 2004; Styczen et al., 2011). Previous studies reported that glyphosate percolates via soil macropores to deeper soil layers (Todorovic et al., 2014) and sometimes to the groundwater during the period of rain (Al-Rajab et al., 2008; Kjaer et al., 2005; Magga et al., 2008; Stone and Wilson, 2006; Ulén et al., 2012). However, extreme experiment in this study presented that most of the glyphosate remained in top soil layer (0–2 cm) rather than in deep soil layers (2–5 and 5–10 cm), consistent with other findings (Laitinen et al., 2009; Zablutowicz et al., 2009). The short duration of the rain in this study undoubtedly contributed to the observed levels of the leachates but leaching via the whole soil depth wasn't observed attributing to the limit depth of soil infiltration ( $<15 \text{ cm}$ ). The risk of glyphosate leaching, however, should be explored further, especially in regions where rain and glyphosate application are intensive (Styczen et al., 2011) and groundwater level changes frequently (Borggaard and Gimsing, 2008).

What's more, tracing and evaluating chemicals' footprint are useful for operating related management to control and reduce their risks in environmental system. The results in this simulation study showed that most of the added glyphosate remained in the flume soil, nearly 6-fold more than was transported by the runoff and suspended load, suggesting that a large proportion of applied glyphosate remains onsite and can contaminate agricultural soils (Sprankle et al., 1975) and can potentially pollute neighbouring areas if the soil is eroded again (Todorovic et al., 2014). Concerning the fate of glyphosate, over 90% of the glyphosate, including AMPA, was recovered but approximately 10% of the applied glyphosate was not recovered after such a brief rain. Probably, we filtered the runoff samples before analysis, but calculating the proportions of the dissolved and particulate-bound fractions in runoff suspensions can be difficult. Glyphosate can also be ejected from the flumes during the simulated rain, although the amount would likely be small (Borggaard and Gimsing, 2008; Gjettermann et al., 2011). Some of the glyphosate may have decayed in this loess soil, and degradation products other than AMPA may not be detected (Bergström et al., 2011). Thus, further study needs to be done in order to understand glyphosate degradation process in Chinese loess soil with/without erosion issues.



**Fig. 4.** Glyphosate fate in short-term simulation rainfall of treatments.

**Table 5**  
Glyphosate transport with runoff and sediment in the first hour after application.

Treatment	Applied glyphosate (mg m <sup>-2</sup> )	Glyphosate transported by runoff <sup>a</sup> (mg m <sup>-2</sup> )				Glyphosate transported by suspended load <sup>a</sup> (mg m <sup>-2</sup> )				Sum (mg m <sup>-2</sup> )	Transport rate (% h <sup>-1</sup> )
		∑ 15 min	∑ 30 min	∑ 45 min	∑ 60 min	∑ 15 min	∑ 30 min	∑ 45 min	∑ 60 min		
T1	360	7.24	10.39	12.14	13.36	17.90	28.07	35.56	42.36	55.72	15%
T2	360	7.30	10.14	11.78	12.99	22.70	32.10	37.20	41.19	54.19	15%
T3	720	14.25	20.84	26.80	29.72	23.88	41.36	51.79	59.81	89.54	12%
T4	720	18.00	25.78	29.85	33.36	28.46	42.90	53.08	60.69	94.05	13%

<sup>a</sup> The amount of AMPA was calculated as parent glyphosate according to molecular mass.

## 5. Conclusions

Glyphosate being applied before and after sowing to bare loess soil leads to strong risk for offsite transport if rainfall occurs shortly after the application. Particulate-facilitated transport is the main mode for glyphosate contaminating offsite. The risk of glyphosate retained in top soil is high and the efforts on reducing contamination in offsite need to be taken where soil erosion happens frequently. The possible effective solution for the dissolved and particle-facilitated transport of pollutants is "buffer zone" which is referred as the protection area for ecosystem discharge (Luijendijk et al., 2003; Passeport et al., 2014; Syversen and Bechmann, 2004). In order to reduce the risk of glyphosate offsite, several practical works or guidelines can be considered: 1) spraying glyphosate properly without any intensive rainfall, especially in erosion regions; 2) extending furrows or ridges avoiding water and soil directly entering water system; and 3) setting protection area located between farming land and public rivers. Therefore, further work to fill the gap of glyphosate fate in loess soil, as well as the efficiency of "buffer zone" under field condition should be considered.

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