



Decay characteristics and erosion-related transport of glyphosate in Chinese loess soil under field conditions



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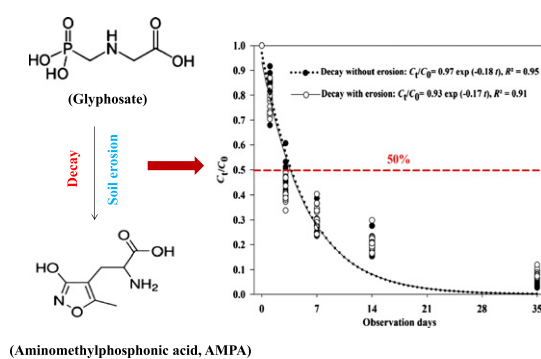
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HIGHLIGHTS

- The characteristics of glyphosate decay were studied in Chinese loess soil.
- Glyphosate decayed rapidly with 3.5 d of half-life in topsoil of field plots.
- Glyphosate and AMPA residuals mainly concentrated in the upper 2 cm of the soil.
- Intense rains contribute to the occurrence of glyphosate and AMPA offsite.

GRAPHICAL ABSTRACT



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ABSTRACT

The decay characteristics and erosion-related transport of glyphosate and aminomethylphosphonic acid (AMPA) were monitored for 35 d at different slope gradients and rates of application in plots with loess soil on the Loess Plateau, China. The initial glyphosate decayed rapidly (half-life of 3.5 d) in the upper 2 cm of soil following a first-order rate of decay. AMPA content in the 0–2 cm soil layer correspondingly peaked 3 d after glyphosate application and then gradually decreased. The residues of glyphosate and AMPA decreased significantly with soil depth ($p < 0.05$) independently of the slope inclination and application rate. About 0.36% of the glyphosate initially applied was transported from plots after one erosive rain 2 d after the application. Glyphosate and AMPA concentrations in runoff were low while the contents in the sediment were much higher than in the upper 2 cm of the soil.

Capsule: Although the rate of glyphosate decay is rapid in Chinese loess soil, the risks of glyphosate and AMPA need to be taken into account especially in the area with highly erosive rainfall.

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1. Introduction

Agrochemical products have contributed substantially to the increase in crop production. Contaminated environmental systems and threatened food safety, the unexpected consequences of pesticide application, however, have become worldwide issues in recent decades (Geissen et al., 2010; Richards and Baker, 1993; Ruiz-Suarez et al., 2014). Pesticides applied to farmland can accumulate onsite or be transported offsite during the process of decay (Glotfelty et al., 1984; Melgar et al., 2008; Ongley et al., 2010). Pesticide registration, production, and application are thus supervised and even restricted based on the physicochemical properties, i.e. the molecular forms, water solubility, decay pattern, and metabolites, and on the ecotoxicology in ecosystems and human health (Perry et al., 2014).

Glyphosate (N-(phosphonomethyl)glycine; $C_3H_8NO_5P$), a highly efficient broad-spectrum and non-selective herbicide, has been used widely in agriculture (Wojtaszek et al., 2004), especially in glyphosate-tolerant crops (Liphadzi et al., 2005). Repeated application and unpredictable mixtures with other pesticides increase the incidence of glyphosate and its metabolic residues in soils (Al-Rajab et al., 2008; Bergstrom et al., 2011; Borggaard and Gimsing, 2008; Kilbride and Paveglio, 2001; Simonsen et al., 2008), sediments (Akamatsu et al., 2014; Degenhardt et al., 2012; Todorovic et al., 2014), plants (roots) (Al-Rajab and Schiavon, 2010; Mamy et al., 2010; Sprankle et al., 1975), and surface/groundwater (Coupe et al., 2012; Huang et al., 2004; Passeur et al., 2014; Van Stempvoort et al., 2014). Glyphosate is a polyprotic acid that can occur as mono- and divalent anions with high affinity for trivalent cations such as aluminium and ferric ions (Barja and Afonso, 2005; Sheals et al., 2002). Gimsing et al. (2004) reported that <2% of the residues were bioavailable the day after the application of glyphosate to six Danish surface soils, whereas >50% of the glyphosate was adsorbed to iron and aluminium oxides. Glyphosate, an organophosphate herbicide, binds to the soil in a manner similar to natural organophosphate compounds, with ligand exchange through the phosphonic acid moiety (Al-Rajab et al., 2008; Sheals et al., 2002; Sprankle et al., 1975). The competition between the similar adsorption sites of glyphosate and phosphates, however, has a severe impact on glyphosate binding and hence on its mobility in soils (Borggaard and Gimsing, 2008; Zhao et al., 2009). The pH and the amounts of variable charges, clay fractions, and soil organic matter also influence the adsorption capacity of glyphosate in soils, which ranges from 62 to 2751 $L\ kg^{-1}$ (Al-Rajab et al., 2008; Albers et al., 2009; Bergstrom et al., 2011; Gimsing and Borggaard, 2002; Gimsing et al., 2004; Gjettermann et al., 2011; Rampazzo et al., 2013; Sprankle et al., 1975; Strange-Hansen et al., 2004; Wang et al., 2005, 2006; Zhao et al., 2009). The variation of adsorption capacity in soils illustrates that glyphosate mobility is variable, and the risks of transport should be taken into account, especially in soils with high phosphate contents from the excessive application of phosphorus fertilisers (Borggaard and Gimsing, 2008).

The pesticides used in agriculture should protect the crops but should also be environmentally safe, which is related to the decay of the pesticides to compounds with low or no toxicity (Perry et al., 2014). Biodegradation by microflora plays an important role in glyphosate decay (Liphadzi et al., 2005; Schroll et al., 2006). The biodegradation of glyphosate in soil follows two pathways: the oxidative cleavage of the C–N bond to yield aminomethylphosphonic acid (AMPA) and the breaking of the C–P bond to generate sarcosine (Borggaard and Gimsing, 2008). The efficiency of biodegradation can be enhanced by providing suitable conditions for the reproduction of introduced microorganisms (Shushkova et al., 2010). The factors that determine the occurrence and degree of decay of glyphosate in the environment, however, remain to be clarified (Borggaard and Gimsing, 2008). The half-life (DT_{50}) of glyphosate in soil varies from 1.7 to 197.3 d depending on soil properties and experimental conditions (Al-Rajab and Hakami, 2014; Bergstrom et al., 2011; Giesy et al., 2000;

Litz et al., 2011; Mamy et al., 2005; Sorensen et al., 2006; Yang et al., 2013). The characteristics of glyphosate decay in different types of soil thus require further study to quantify the potential risks to, or the effects on, the surrounding environments.

The “Birch effect”, a pulse in the mineralisation of soil carbon and nitrogen by wetting (Birch 1958), increases the mineralisation of previously unavailable substances, especially for the decomposition of organic substrates (Borken and Matzner, 2009; Lado-Monserrat et al., 2014). The dynamics of soil moisture caused by heavy rains would likely indirectly affect glyphosate decay and transport with preferential flow (Coupe et al., 2012; Degenhardt et al., 2012; Todorovic et al., 2014), which would increase the risk to nearby water bodies, soils, and aquatic life (Avigliano et al., 2014; Lanctot et al., 2013; Londo et al., 2014; Webster et al., 2014). Erosive rainfall occurs frequently in regions with loess soil in China (Shi and Shao, 2000), and many nutrients and pesticides are transported, leading to serious water pollution (Li et al., 2011; Ongley et al., 2010). Glyphosate in soil either can be dispersed in runoff and drainage or carried with soil particles (Avigliano et al., 2014; Bergstrom et al., 2011; Kjaer et al., 2005; Lanctot et al., 2013; Londo et al., 2014; Styczen et al., 2011; Webster et al., 2014). Many studies have documented the transport of glyphosate by runoff and leached discharge, but most have focused on laboratory and lysimetric methods using pots or soil columns (Bergstrom et al., 2011; Zhao et al., 2009; Zhou et al., 2010). In China, glyphosate is applied to bare soil before and after sowing every year (Yang et al., 2014; Zhang et al., 2011), which underlies a high risk of transport by processes associated with erosion (Al-Rajab and Schiavon, 2010; Laitinen et al., 2009; Styczen et al., 2011; Todorovic et al., 2014). Furthermore, few studies have examined the decay or transport of glyphosate under field or erosive conditions in Chinese loess soil, especially in semi-humid climatic regions (Newton et al., 2008). Identifying the characteristics of decay with/without erosive rainfall, including the dynamics of soil moisture, is particularly important. The aims of the present study were thus, to (1) monitor glyphosate decay with/without erosive rainfall under field conditions in Chinese loess soil and (2) quantify the transport of glyphosate and its metabolite AMPA by eroded materials to assess the risk of onsite accumulation and offsite pollution.

2. Materials and methods

2.1. Study area

This study was conducted in a field monitoring station in Yangling, Shaanxi Province, China ($34^{\circ}16'N$, $108^{\circ}04'E$). The climate is semi-humid with a mean annual temperature of $12.9^{\circ}C$ and maximum and minimum temperatures of 42 and $-19.4^{\circ}C$, respectively. The mean annual precipitation is 610 mm, with a rainy season from July to October. The annual evaporation is 1505 mm. The wind is usually from the east or west with a maximum speed of $21.7\ m\ s^{-1}$. The dominant soil type is loess which has been disturbed by intensive anthropogenic activity (Nachtergaele et al., 2000) (Table 1).

2.2. Experimental design

2.2.1. Decay and transport of glyphosate

The commercial product Roundup® (Monsanto, Sinochem International Corporation (agent)) containing 360 g acid equivalent L^{-1} glyphosate as an isopropylamine salt was selected for the experiment (Yang et al., 2014). Glyphosate was sprayed at two rates: $3.6\ kg\ a.i.\ ha^{-1}$ (G1), commonly used in fields along channels/rivers, and $7.2\ kg\ a.i.\ ha^{-1}$ (G2), to simulate an extreme case. The experiment was conducted in $20\ m \times 1.67\ m$ plots each at two slope inclinations (10° (S1) and 20° (S2)). Each treatment was replicated three times, for a total of 12 plots.

Plastic sheets 40 cm in width were buried vertically into the soil to avoid the infiltration and dispersion of the pesticide in the subsurface soil. Each plot was surrounded by a ridge 5 cm in height to prevent

Table 1
Soil properties in experimental plots ($n = 12$).

Properties	Soil depth (cm)		
	0–2	2–5	5–10
Particle size distribution:			
<0.002 mm (clay) (%)	29.8 ± 1.3	30.2 ± 2.2	29.7 ± 2.0
0.002–0.02 mm (%)	41.2 ± 2.3	41.5 ± 2.0	41.3 ± 2.4
0.02–2 mm (%)	27.2 ± 2.1	26.4 ± 1.8	26.6 ± 1.8
>0.2 mm (%)	1.8 ± 0.1	2.0 ± 0.2	2.2 ± 0.1
Bulk density (g cm^{-3})	1.2 ± 0.1	1.2 ± 0.1	1.4 ± 0.1
pH(H_2O)	7.9 ± 0.02	8.0 ± 0.04	8.0 ± 0.03
EC ($\mu\text{S cm}^{-1}$)	143.4 ± 5.1	134.5 ± 2.3	142.1 ± 1.6
Cation exchange capacity (CEC) (cmol kg^{-1})	19.2 ± 2.3	18.3 ± 1.4	18.3 ± 1.8
Organic matter (g kg^{-1})	5.1 ± 0.1	5.4 ± 0.1	5.62 ± 0.1
Total phosphorous (g kg^{-1})	0.6 ± 0.01	0.7 ± 0.02	0.7 ± 0.02
Available phosphorous-Olsen (mg kg^{-1})	14.4 ± 1.2	15.0 ± 1.0	11.1 ± 1.0
Total Al total (g kg^{-1})	27.6 ± 2.1	26.1 ± 1.9	25.9 ± 2.1
Total Fe (g kg^{-1})	32.0 ± 1.8	30.7 ± 2.3	30.3 ± 1.9

the exchange of overland flow between plots. The plots were then ploughed, and smoothed along the slope. The experiment was conducted from September to October 2012 and from July to August 2013. In 2012, we studied glyphosate decay without the influence of erosive rainfall. In 2013, we additionally studied glyphosate transport by runoff and eroded materials, because erosive rain fell during this

period. Glyphosate was sprayed on the bare soil surface of each plot in 2012 and 2013 using a hand-operated sprayer equipped with a 2-m wand at a nozzle pressure of 0.25 Mpa and a nozzle distance of 5 cm above the soil surface. The nozzle was protected by a cover to prevent the dispersal of the glyphosate solvent by winds. The wind speed was monitored during spraying to avoid glyphosate drift and the contamination of adjacent plots. Channels for discharging runoff and sediment were also added to the ends of each plot in 2013. Buckets with 40 cm diameter were connected with plastic pipes from the discharge channels. Groups of three plots were considered as triple replicates.

2.2.2. Sampling

In 2012, soil samples were collected in a metallic auger from the ploughed layer (0–2, 2–5, and 5–10 cm) on the day but before glyphosate application (background information of glyphosate/AMPA residues) and on days 1, 3, 7, 14, and 35 after application. Each sample was stored separately, and the auger was cleaned between samples.

In 2013, soil samples were only collected from the 0–2 cm layer due to the results of 2012. In 2013, samples of runoff and sediment were also collected after one erosive rainfall (44.5 mm). The mixed runoff and sediment from each plot were stirred thoroughly in the buckets and sampled as soon as possible in plastic bottles. The samples were then weighed and allowed to settle in the laboratory for 2 h. The supernatants were decanted and stored in 100-mL plastic bottles, and the sediments were dried in the shade for 48 h. Each solid sample was transferred to a plastic bag and subdivided into two parts: one for soil

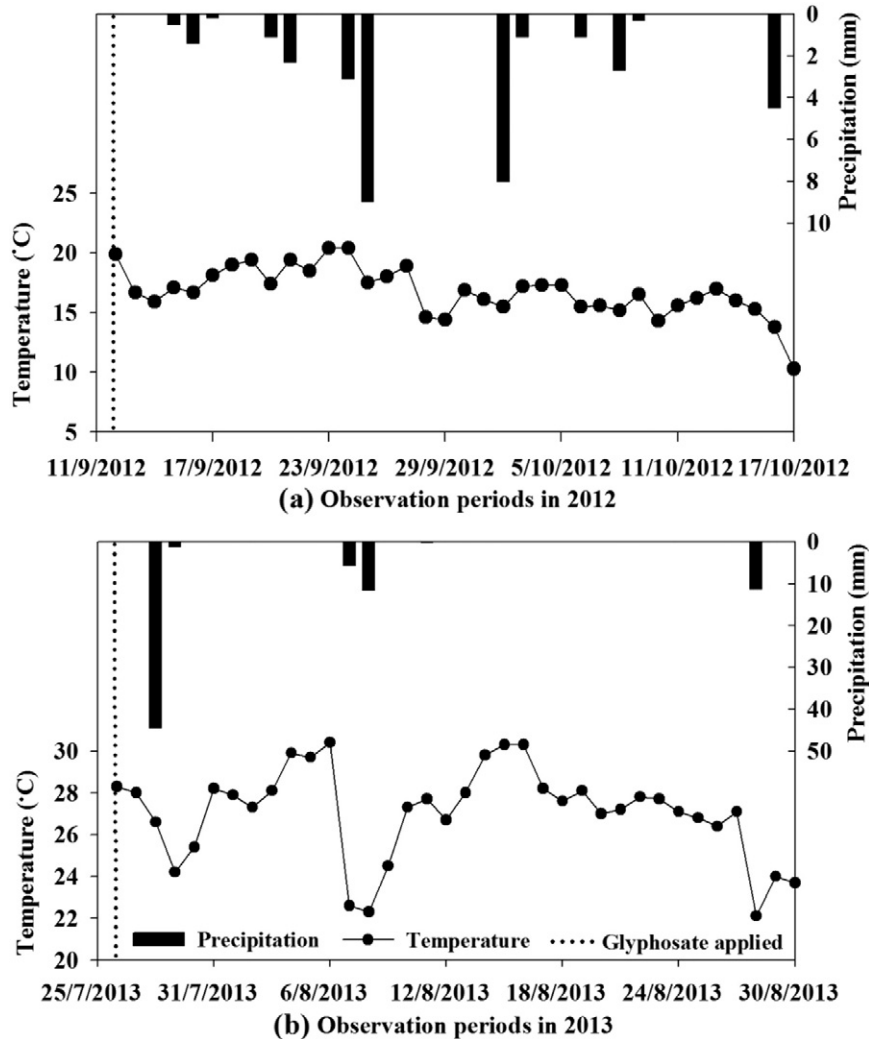


Fig. 1. Precipitation and temperature of monitoring periods in 2012 (a) and 2013 (b).

moisture and one for glyphosate determination. All samples were stored at $-24\text{ }^{\circ}\text{C}$ until analysis.

2.3. Glyphosate and AMPA analysis

2.3.1. Chemicals

Glyphosate (98%), AMPA (98.5%), sodium tetraborate decahydrate ($\geq 99.5\%$), and ammonium acetate (approx. 98%) were purchased from Sigma-Aldrich Co. (USA). Isotopically labelled glyphosate ($1,2\text{-}^{13}\text{C}$, ^{15}N ; $100\text{ }\mu\text{g mL}^{-1}$; 1.1 mL) and AMPA (^{13}C , ^{15}N ; $100\text{ }\mu\text{g mL}^{-1}$; 1.1 mL), used as internal standards, were obtained from Dr. Ehrenstorfer (Augsburg, Germany). FMOC-Cl (9-fluorenylmethoxycarbonyl chloride) ($\geq 99.0\%$) was purchased from Sigma-Aldrich (Switzerland). Potassium hydroxide (KOH) (p.a., 85%), hydrochloric acid (HCl) (37%), and ammonia solution (25%) were purchased from Merck KGaA (Darmstadt, Germany). Methanol (MeOH) and acetonitrile (HPLC grade) were purchased from Actua-All Chemicals (The Netherlands). Formic acid (p.a., $\geq 98\%$) was obtained from Gevaar (The Netherlands).

2.3.2. Extraction and derivatization

Glyphosate was extracted in tubes from 2 g of each soil and sediment sample with 10 mL of 0.6 M KOH and then one millilitre of the supernatant was transferred to adjust pH value before derivatization (Yang et al., 2015). For the runoff samples, 1 mL of the sample was directly transferred to a 10-mL plastic tube and immediately derivatized. The derivatization step was the same for all samples (soil, runoff, and sediment) as described by Yang et al. (2015). All samples were prepared in duplicate. Solvent standards were freshly derivatized together with the samples for each batch of samples. Then glyphosate and AMPA concentrations were determined by liquid chromatography–tandem mass spectrometry using an XBridge™ Shield RP C18 column, $3.5\text{ }\mu\text{m}$ particle size, $150\text{ mm} \times 2.1\text{ mm}$ i.d. column (Waters, The Netherlands). All the parameters of methods were described by Yang et al. (2015).

2.4. Data analysis

The means and standard deviations for all glyphosate and AMPA concentrations were calculated. We assumed that glyphosate residues in the soil prior to the experiment did not decay during monitoring. The theoretical concentrations of applied glyphosate (C_0 , $\mu\text{g g}^{-1}$) in the upper 2 cm of soil were $15\text{ }\mu\text{g g}^{-1}$ for treatments S1G1 and S2G1 and $30\text{ }\mu\text{g g}^{-1}$ for S1G2 and S2G2, calculated by:

$$C_0 = \frac{m \times 1000}{A \times d \times \rho_b} \quad (1)$$

where m is the total amount of applied glyphosate, mg; A is the plot area, m^2 ; d is the soil depth, m; and ρ_b is the soil bulk density, kg m^{-3} .

All treatments were treated as replicates, and the regression curve for the detected glyphosate plotted against the initially applied glyphosate in the soil was determined for each year. The amount of decay and half-life were then determined by the first-order exponential decay of glyphosate residues in the soil as:

$$\frac{C_t}{C_0} = e^{-kt} \quad (2)$$

where C_t is the content of glyphosate t days after application, $\mu\text{g g}^{-1}$; C_0 is the rate of glyphosate decay during the observation days, unitless; and k is the first-order rate coefficient for degradation, t^{-1} . Then the half-life of glyphosate (DT_{50}) in soil can then be calculated:

$$DT_{50} = \frac{\ln 2}{k} \quad (3)$$

The total amount of glyphosate transported (T_{loss} , kg ha^{-1}) was calculated from the runoff and sediment:

$$T_{\text{loss}} = \frac{\sum (C_{rg} \times V + 1.52 \times C_{ra} \times V) + \sum (C_{sg} \times m_s + 1.52 \times C_{sa} \times m_s)}{10^6} \quad (4)$$

where C_{rg} is the glyphosate concentration of the runoff, $\mu\text{g mL}^{-1}$; C_{sg} is the glyphosate content of the sediment, $\mu\text{g g}^{-1}$; C_{ra} is the AMPA concentration of the runoff, $\mu\text{g mL}^{-1}$; C_{sa} is the AMPA content of the sediment, $\mu\text{g g}^{-1}$; m_s is the sediment weight, kg ha^{-1} ; and V is the runoff volume, L ha^{-1} ; 1.52 is the coefficient of AMPA calculated as parent glyphosate according to molecular mass. Meanwhile, pesticide sediment-runoff partition coefficient (K_p , L kg^{-1}) was calculated as the content of glyphosate/AMPA in the sediment divided by concentration of pesticide in the runoff.

The rate of loss of glyphosate during an erosive rain (R_{loss}) is:

$$R_{\text{loss}} (\%) = \frac{T_{\text{loss}}}{T} \times 100\% \quad (5)$$

where T is the initial amount of glyphosate applied, $3.6\text{ kg a.i. ha}^{-1}$ or $7.2\text{ kg a.i. ha}^{-1}$ in this study.

The data were tested for normality with the Kolmogorov–Smirnov test ($p < 0.05$). Analyses of variance followed by Tukey tests tested for significant differences between treatments ($p < 0.05$). Fisher's least significant difference (LSD) tests compared the differences of glyphosate and AMPA content in the soil layers ($p < 0.05$). The best fit curve for glyphosate decay was estimated and graphed by SigmaPlot 10.0. The statistical analyses were performed using SPSS 20.0.

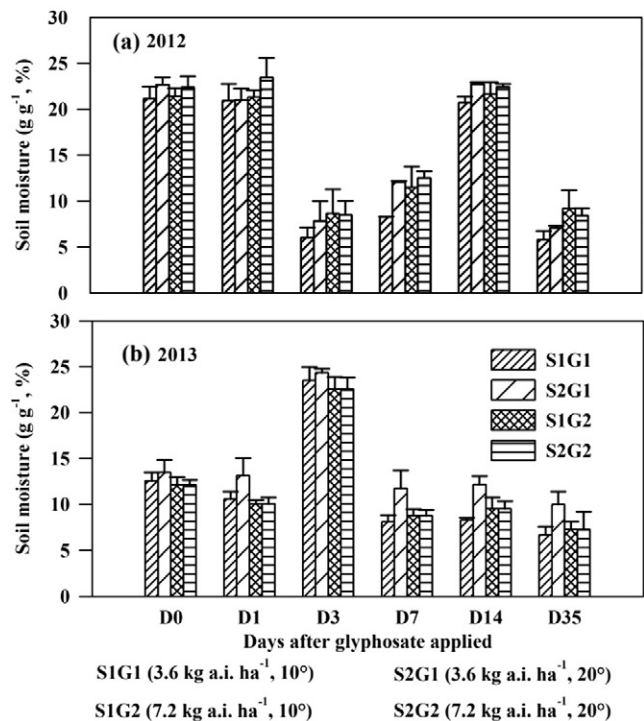


Fig. 2. Soil moisture in upper 2 cm soil days after glyphosate application in 2012 (a) and 2013 (b).

Table 2
Glyphosate residues in different soil layers of the different treatments (2012).

Treatment	Soil depth (cm)	Glyphosate residues before and after days from application ($\mu\text{g g}^{-1}$)					
		0 [#]	1	3	7	14	35
S1G1	0–2	0.36 ± 0.01 a	12.11 ± 1.13 a	6.33 ± 0.42 a	4.89 ± 0.78 a	3.50 ± 0.60 a	0.52 ± 0.10 a
	2–5	0.02 ± 0.01 b*	0.03 ± 0.01 b	0.11 ± 0.01 b	0.02 ± 0.00 b*	0.20 ± 0.12 b*	0.03 ± 0.00 b
	5–10	0.04 ± 0.01 b	0.06 ± 0.03 b	0.03 ± 0.01 b	0.01 ± 0.00 b*	0.06 ± 0.03 b	0.02 ± 0.01 b*
S2G1	0–2	0.35 ± 0.11 a	12.14 ± 1.71 a	7.59 ± 0.12 a	4.36 ± 0.73 a	2.47 ± 0.18 a	0.64 ± 0.11 a
	2–5	0.03 ± 0.01 b	0.07 ± 0.03 b	0.04 ± 0.01 b	0.09 ± 0.05 b	0.02 ± 0.01 b*	0.01 ± 0.00 b*
	5–10	0.05 ± 0.01 b	0.09 ± 0.01 b	0.02 ± 0.00 b*	0.03 ± 0.00 b	0.01 ± 0.00 b*	0.01 ± 0.00 b*
S1G2	0–2	0.64 ± 0.10 a	25.28 ± 0.28 a	12.65 ± 0.82 a	7.79 ± 0.50 a	6.41 ± 0.59 a	0.96 ± 0.07 a
	2–5	0.10 ± 0.01 b	0.03 ± 0.01 b	0.03 ± 0.00 b	0.05 ± 0.05 b	0.02 ± 0.00 b*	0.01 ± 0.00 b*
	5–10	0.07 ± 0.01 b	0.05 ± 0.02 b	0.04 ± 0.03 b	0.02 ± 0.02 b*	0.01 ± 0.01 b*	0.01 ± 0.00 b*
S2G2	0–2	0.56 ± 0.21 a	26.02 ± 1.53 a	15.94 ± 2.23 a	7.88 ± 1.11 a	6.26 ± 0.84 a	1.42 ± 0.25 a
	2–5	0.12 ± 0.02 b	0.04 ± 0.02 b	0.05 ± 0.02 b	0.13 ± 0.03 b	0.01 ± 0.00 b*	0.01 ± 0.00 b*
	5–10	0.07 ± 0.01 b	0.02 ± 0.01 b*	0.03 ± 0.01 b	0.01 ± 0.00 b*	0.01 ± 0.01 b*	0.01 ± 0.00 b*

Different lowercase letters mean significant difference between the soil layers at the same time ($p < 0.05$).
 S1G1 (3.6 kg a.i. ha⁻¹, 10°); S2G1 (3.6 kg a.i. ha⁻¹, 20°); S1G2 (7.2 kg a.i. ha⁻¹, 10°); S2G2 (7.2 kg a.i. ha⁻¹, 20°).
 * Means the results lower than the detection limit.
 # Means the residues of glyphosate in soil layers on the day before glyphosate applied.

3. Results

3.1. Dynamic change of precipitation, temperature, and soil moisture

The total amounts of precipitation were 35.3 and 74.3 mm during the 35-d monitoring periods in 2012 and 2013, respectively (Fig. 1). In 2012, no erosive rains fell during the monitoring period, which had an average temperature of 16.8 ± 2.1 °C (Fig. 1a). In 2013, only one erosive rain fell on 28 July, 2 d after the glyphosate was applied. The erosive rain was 44.3 mm within 80 min, and the intensity was 33.4 mm h⁻¹. The average temperature in July–August 2013 was 27 ± 2.3 °C (Fig. 1b). Soil moisture in the surface layer (0–2 cm) correspondingly changed when it rained but did not vary at different slopes (Fig. 2). The initial soil moisture was higher in 2012 than in 2013, and dynamic changes were observed due to the rain (Fig. 2a,b).

3.2. Glyphosate decay

3.2.1. Glyphosate and AMPA residues

Glyphosate and AMPA were detected in all soil samples from all layers in 2012 (Tables 2 and 3). Glyphosate and AMPA concentrated in the 0–2 cm soil layers of the treatments and some of glyphosate and AMPA, however, were below the limits of detection in the deeper soil layers (2–5 and 5–10 cm) ($p < 0.05$). Interestingly, some AMPA was detected in deeper soil before and after the glyphosate was applied in S1G2 and S2G2, although the contents were lower than those in the

0–2 cm soil layers. Glyphosate residues in the upper 2 cm of soil decreased rapidly in the first 3 d and then decreased gradually (Table 2), while the AMPA content increased in the first 3 d and then decreased (Table 3). Similarly, the glyphosate and AMPA content differed for the two rates of application, at least in the upper 2 cm of soil, but not significantly for the different slopes with the same rate of glyphosate treatment.

3.2.2. The characteristics of glyphosate decay

Glyphosate residues in soil (0–2 cm) followed exponential decay curve, regardless of the rate of glyphosate application, slope, and the occurrence of erosion (Fig. 3). Glyphosate decayed rapidly in the first three days and then its residues varied slightly, especially 21 d after glyphosate applied. Furthermore, the exponential decay-rate constant was similar while the intercepts of the regression equations for S1G1 and S2G1 were nearly half those for S1G2 and S2G2 attributing to the initial rate of glyphosate applied. The constant and intercept of regression equations differed slightly between 2012 (Fig. 3a) and 2013 (Fig. 3b) at the same treatment. Interestingly, the intercepts of the regression equations in different treatments were close to the initial amount of added glyphosate. Supposedly, there was no drift and loss on the day when glyphosate was sprayed. In the best fit regression curve of the glyphosate decay data are shown in Fig. 4 ($p < 0.01$, $n = 72$):

$$\frac{C_t}{C_0} = 0.97 e^{-0.18 t} \quad (p < 0.01, R^2 = 0.95, n = 72) \quad (6)$$

Table 3
AMPA residues in different soil layers of the different treatments (2012).

Treatment	Soil depth (cm)	AMPA residues before and after days from application ($\mu\text{g g}^{-1}$)					
		0 [#]	1	3	7	14	35
S1G1	0–2	1.91 ± 0.18a	3.23 ± 0.46a	6.14 ± 0.40a	5.37 ± 1.46a	4.64 ± 0.65a	2.62 ± 0.52a
	2–5	0.06 ± 0.01b	0.25 ± 0.06b	0.22 ± 0.04b	0.30 ± 0.08b	0.41 ± 0.12b	0.15 ± 0.03b
	5–10	0.05 ± 0.01b	0.13 ± 0.01b	0.12 ± 0.04b	0.09 ± 0.03b	0.17 ± 0.02b	0.17 ± 0.07b
S2G1	0–2	1.43 ± 0.17a	2.86 ± 0.92a	5.48 ± 0.95a	4.10 ± 0.48a	2.74 ± 0.22a	1.74 ± 0.23a
	2–5	0.03 ± 0.01b*	0.06 ± 0.01b	0.05 ± 0.00b	0.22 ± 0.16b	0.08 ± 0.01b	0.04 ± 0.02b
	5–10	0.04 ± 0.00b	0.10 ± 0.03b	0.03 ± 0.01b*	0.06 ± 0.04b	0.04 ± 0.01b	0.04 ± 0.01b
S1G2	0–2	2.91 ± 0.34a	5.27 ± 0.02a	12.60 ± 0.67a	7.39 ± 0.26a	4.48 ± 0.40a	4.19 ± 0.52a
	2–5	0.76 ± 0.17b	0.07 ± 0.03b	0.61 ± 0.06b	0.90 ± 0.12b	0.17 ± 0.06b	0.23 ± 0.10b
	5–10	0.55 ± 0.21b	0.08 ± 0.01b	0.19 ± 0.07b	0.10 ± 0.02c	0.17 ± 0.09b	0.08 ± 0.02c
S2G2	0–2	2.62 ± 0.22a	5.44 ± 0.23a	10.73 ± 0.45a	7.41 ± 0.20a	5.19 ± 0.52a	3.72 ± 0.40a
	2–5	0.66 ± 0.01b	0.21 ± 0.02b	0.16 ± 0.04b	0.07 ± 0.01b	0.76 ± 0.36b	0.06 ± 0.01b
	5–10	0.35 ± 0.01b	0.04 ± 0.00c	0.04 ± 0.01b	0.04 ± 0.02b	0.07 ± 0.00c	0.03 ± 0.00b*

Different lowercase letters mean significant difference between the soil layers at the same time ($p < 0.05$).
 S1G1 (3.6 kg a.i. ha⁻¹, 10°); S2G1 (3.6 kg a.i. ha⁻¹, 20°); S1G2 (7.2 a.i. kg ha⁻¹, 10°); S2G2 (7.2 kg a.i. ha⁻¹, 20°).
 * Means the results lower than the detection limit.
 # Means the residues of AMPA in soil layers on the day before glyphosate applied.

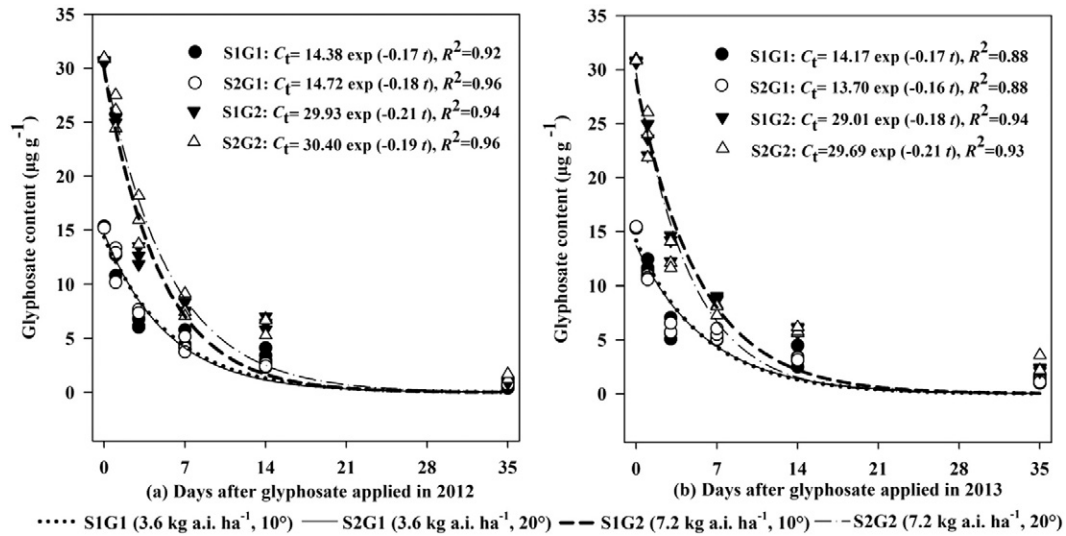


Fig. 3. Glyphosate content in upper 2 cm soil at the first 35 d after application in different treatments: (a) 2012 and (b) 2013.

$$\frac{C_t}{C_0} = 0.93 e^{-0.17t} \quad (p < 0.01, R^2 = 0.91, n = 72). \quad (7)$$

The coefficients of the equations regressed in Fig. 4 were similar, even though 2013 had one erosive rainfall (Eq. (6)). Thus, the simple model to Eq. (2) for glyphosate decay in Chinese loess soil can be expressed as:

$$\frac{C_t}{C_0} = e^{-0.2t} \quad (p < 0.01, R^2 = 0.93, n = 144). \quad (8)$$

From this model, it showed that glyphosate decayed relatively rapidly with a DT_{50} of 3.5 d in loess soil. The comparison of glyphosate residues predicted by Eq. (8) was scattered and fitted well with the observed contents in 2012 and 2013 (Fig. 5). Accordingly, in the upper 2 cm soil, AMPA content peaked on the third day after glyphosate application (Fig. 6). The AMPA content then gradually decreased following the exponential decay curve, and significant differences were observed between the treatments at the different rates of glyphosate application ($p < 0.05$). However, AMPA content did not differ significantly between the different slopes at the same rate of glyphosate application.

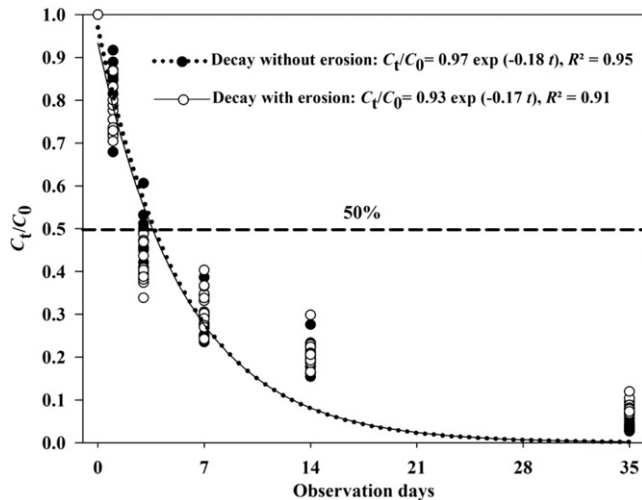


Fig. 4. The rate of glyphosate residues (C_t/C_0) in upper 2 cm soil during 35 d.

3.3. Glyphosate transport

2013 had only one erosive rainfall (44.5 mm within 80 min) during the 35-d monitoring period, 2 d after glyphosate application. The runoff and erosion rates, ranging from 0.21 to $0.38 \times 10^{-4} \text{ L ha}^{-1}$ and from 0.015 to $0.025 \times 10^{-4} \text{ kg ha}^{-1}$, respectively, varied but did not differ significantly between S1 and S2. The glyphosate and AMPA contents in the runoff and sediments depended significantly on the rate of glyphosate applied ($p < 0.05$). The glyphosate contents were 0.76, 0.87, 1.31, and $1.24 \mu\text{g mL}^{-1}$ in the runoff and 40.44, 35.21, 71.85, and $58.95 \mu\text{g g}^{-1}$ in the sediments in the S1G1, S2G1, S1G2, and S2G2 treatments, respectively. Similarly, AMPA contents were significantly higher in the sediments than the runoff. The total transport rate of glyphosate from Eqs. (4) and (5) was similar among the treatments, ranging from 0.31 to 0.46%, with an average of 0.36% of the applied glyphosate transported by runoff and sediments. The sediments transported 71% of the glyphosate, over twice as much as by the runoff. Accordingly, pesticide sediment-runoff partition coefficients (K_p) were 49 ± 7 and $88 \pm 3 \text{ L kg}^{-1}$ for glyphosate and AMPA, respectively. During soil erosion,

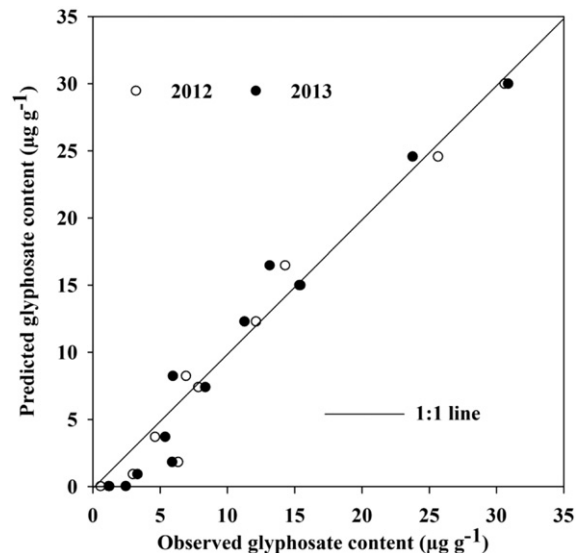


Fig. 5. Predicted (Eq. (8)) vs. observed glyphosate content in upper 2 cm soil.

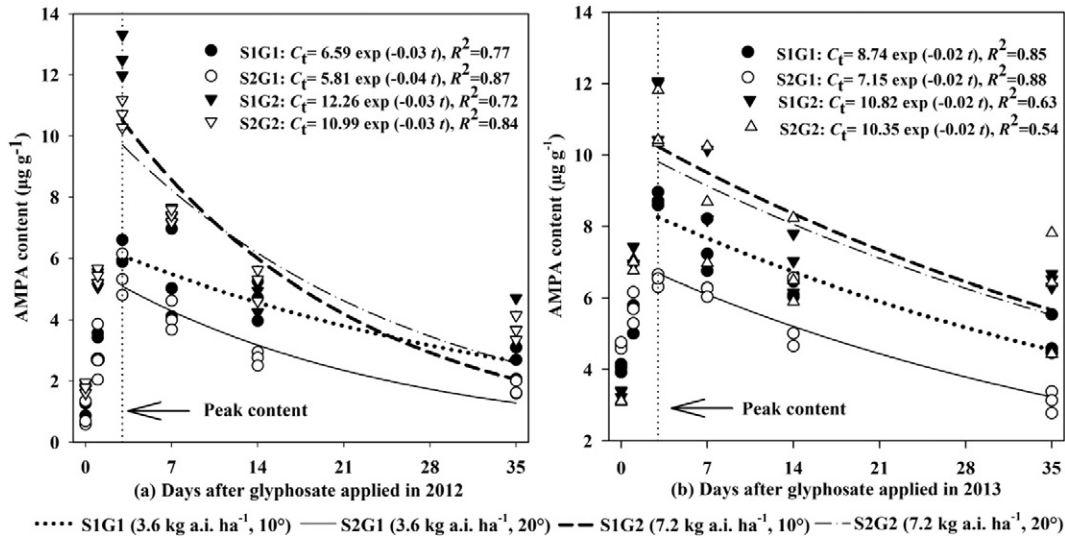


Fig. 6. AMPA content in upper 2 cm soil at the first 35 d after glyphosate application in different treatments: (a) 2012 and (b) 2013.

most of the glyphosate was thus transported bound to soil particles rather than by dispersion in the runoff (Table 4).

4. Discussion

Glyphosate is mobile in various agricultural soils, given that the labile fraction is governed principally by the affinity of the mono- and divalent glyphosate and/or AMPA anions, regardless of depth in the soil profile (Zablotowicz et al., 2009). Bergstrom et al. (2011) reported that the residues of glyphosate and AMPA were mainly detected in topsoil (0–30 cm), despite the application of glyphosate 748 d earlier, and Shushkova et al. (2010) reported that 57% of the glyphosate was concentrated in the 0–10 cm soil layer after 7 d. Studies also showed that glyphosate is initially absorbed mostly in the upper 2 cm of soil rather than transported and absorbed after a few days in deeper soil horizons (Rampazzo et al., 2013) which is similar to Yang et al. (2015) and our results (Tables 2 and 3). Glyphosate and AMPA content then correspondingly decreased significantly in deeper soil layers (2–10 cm) and were even below the limit of detection in some layers.

Precipitation and temperature influence pesticide behaviour and contribute to the effect on soil moisture and the related reactions in the soil matrix (Sorensen et al., 2006). In this study, however, the characteristics of glyphosate decay differed slightly in 2012 and 2013. Probably, the interaction effects of precipitation, temperature and the consequent soil moisture are similar in different two years but further work is needed to verify the factors on glyphosate decay in loess soil.

Table 4
Transport of glyphosate and AMPA with soil erosion.

Observation	Treatments			
	S1G1	S2G1	S1G2	S2G2
Runoff (10 ⁻⁴ L ha ⁻¹)	0.21	0.35	0.24	0.38
Sediment (10 ⁻⁴ kg ha ⁻¹)	0.015	0.025	0.018	0.023
Sediment concentration (kg L ⁻¹)	0.07	0.07	0.08	0.06
Glyphosate concentration in runoff (µg mL ⁻¹)	0.76	0.87	1.31	1.24
AMPA concentration in runoff (µg mL ⁻¹)	0.14	0.12	0.25	0.31
Glyphosate content in sediment (µg g ⁻¹)	40.44	35.21	71.85	58.95
AMPA content in sediment (µg g ⁻¹)	12.08	10.94	21.59	18.08
K _p for glyphosate (L kg ⁻¹)	53.24	40.24	54.79	47.67
K _p for glyphosate (L kg ⁻¹)	84.98	91.53	88.06	86.30
Total amount of glyphosate transport ^a (kg ha ⁻¹)	0.011	0.017	0.023	0.026
Transport rate (%)	0.31	0.46	0.32	0.37

S1G1 (3.6 kg a.i. ha⁻¹, 10°); S2G1(3.6 kg a.i. ha⁻¹, 20°); S1G2(7.2 kg a.i. ha⁻¹, 10°); S2G2(7.2 kg a.i. ha⁻¹, 20°).

^a The amount of AMPA was calculated as parent glyphosate according to molecular mass.

The samples of the upper 2-cm soil layer had higher glyphosate contents in both years corresponding to the applications, with the rates being more significant in the higher than the lower application ($p < 0.05$), probably due to the difference in the applied doses in each case, similar to the results reported by Rampazzo et al. (2013). The simple exponential model was developed to describe glyphosate decay in the loess surface soil (Eq. (8)), fitting with the first-order of chemical decay, in accordance with other studies (Bergstrom et al., 2011; Simonsen et al., 2008). The coefficient k in our study (Eq. (8)), however, was two orders of magnitude larger than those reported by Bergstrom et al. (2011), who used clay soil incubated in the laboratory. The fraction of the variances explained by the R^2 of the nonlinear regression suggests that they provide relevant quantitative information for evaluating glyphosate residues in loess soil. R^2 may be negative for curves describing the formation and degradation of metabolites (Boesten et al., 2005), but the predicted values, including those for both years, were scattered and fitted better with the observed values (Fig. 5).

Concerning the simplified model developed in this study, the half-life of glyphosate in loess soil was 3.5 d, in accordance with those in clay loam soil (Al-Rajab and Schiavon, 2010) but faster than that in sand ($DT_{50} = 16.9$ d) and clay ($DT_{50} = 110$ d) topsoil (Bergstrom et al., 2011). There are several reasons for the differences DT_{50} of glyphosate in studies. One is that the half-life of glyphosate estimated in the laboratory does not realistically reflect glyphosate decay in the field, especially in the dynamic changes of environmental systems (Lancot et al., 2013). Litz et al. (2011) reported a DT_{50} of glyphosate of 30 d, yielding a rate of dissipation of 0.023 d under laboratory conditions at 8 °C, but glyphosate decayed faster at higher temperatures under field conditions, with a half-life of 7.5–10.5 d. Another is that complex interacting processes based on the intrinsic chemical properties of soils also affect glyphosate degradation (Bergstrom et al., 2011; Borggaard and Gimsing, 2008; Laitinen et al., 2009; Pizzul et al., 2009; Sorensen et al., 2006). In this study, the soil type is loess but with lower content of organic matter and higher pH which might increase the possibility of glyphosate decay (De Jonge and De Jonge, 1999; Gimsing et al., 2004). In addition, the half-life of AMPA was also estimated using the sampling time where the content was at maximum (3 d) as the starting point. The results (data not shown) suggested that AMPA decayed with a DT_{50} of 23 d and 35 d in 2012 and 2013, respectively. Although the half-life time of AMPA differed in two years, it indicates that AMPA is more persistent than its parent glyphosate in soil, in accordance with other studies (Al-Rajab et al., 2008; Bergstrom et al., 2011).

Intensive rain-induced soil erosion leads to losses of water and soil that carry nutrients and chemicals, thereby disturbing the balance of the surroundings (Schulz, 2004). In our study, an erosive rainfall was brief, and the intensity was low, leading to low runoff and erosion rates and the consequent less loss of glyphosate, ranging from 0.31 to 0.46% of the applied glyphosate. A large fraction of the transported glyphosate was carried by sediments, in accordance with other studies (Laitinen et al., 2009; Pizzul et al., 2009; Sorensen et al., 2006; Zhou et al., 2010). Relative to the applied glyphosate, the transported glyphosate was limited, but glyphosate and AMPA contents were much higher in the sediments than in the upper 2 cm of soil sampled on the same day, indicating that the runoff and erosion rates under certain conditions determine the amount of glyphosate transported. As it is reported, on the Loess Plateau of China, 40% of the total area (6.2×10^6 ha) suffers severe soil erosion ($>50 \text{ g m}^{-2} \text{ y}^{-1}$) (Chen et al., 2007), and the eroded depth of the surface soil per year is likely >0.04 mm. With this thin layer of eroded soil, chemicals pose great potential risks downstream, especially with frequent erosion and repeated pesticide applications (Zhang et al., 2011). Therefore, further study is needed for monitoring glyphosate/AMPA onsite and offsite in this loss soil area under multiple scenarios (e.g. tillage, irrigation, and erosion control management) and glyphosate applications.

5. Conclusions

The rapid rate of glyphosate decay in Chinese loess soil indicates that the risks of onsite glyphosate pollution and leaching to deeper soil are low. Intense rains are an essential factor for the offsite transport of glyphosate and AMPA and can be a strong risk in regions with high soil erosion rates. Particulate-facilitated transport of glyphosate should receive more attention in the regions where soil erosion frequently occurs. Further study should be considered, and a realistic erosion-pesticide model should be developed that can simulate the particulate-facilitated transport of glyphosate and its offsite risks involving decay processes.

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