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

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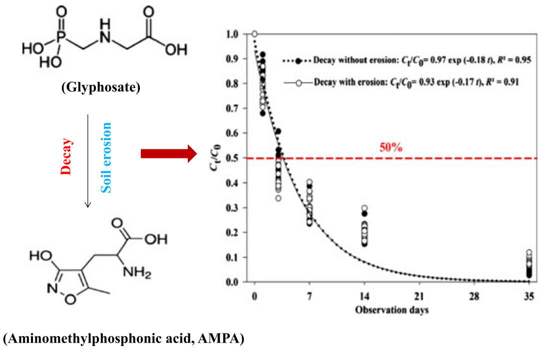
HIGHLIGHTS

- 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; Passeport 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°16′N, 108°04′E). The climate is semi-humid with a mean annual temperature of 12.9 °C and maximum and minimum temperatures of 42 and −19.4 °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 × 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