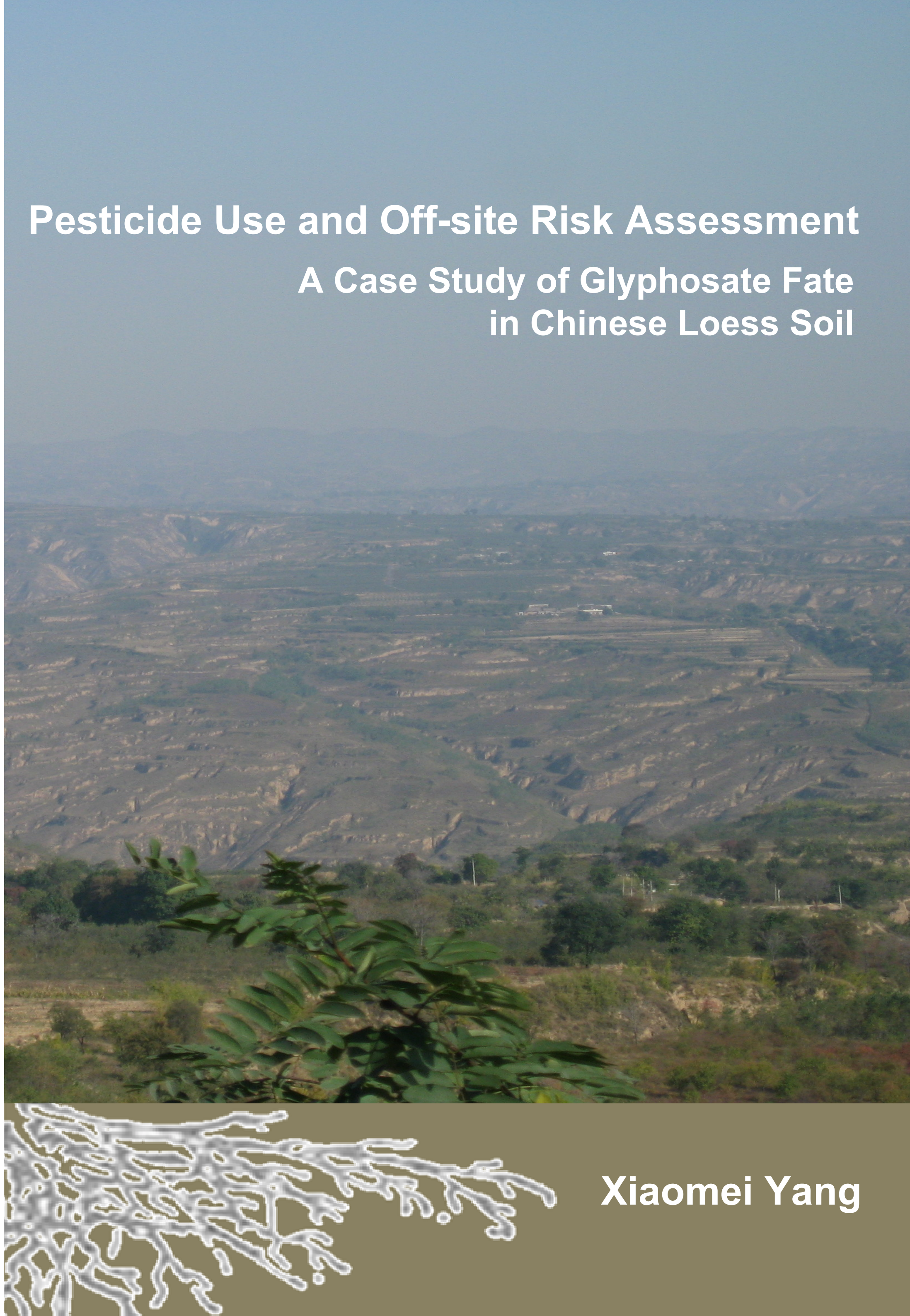
Pesticide Use and Off-site Risk Assessment: A Case Study of Glyphosate in Chinese Loess Soil Xiaomei Yang



Pesticide Use and Off-site Risk Assessment

A Case Study of Glyphosate Fate in Chinese Loess Soil

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1 General introduction

1.1 Fate and risks of pesticides in the environment

Pesticides are compounds that protect crops from pests, diseases and weeds in an effort to reduce or avoid yield losses while maintaining high product quality. Depending on the specific target, the word pesticides can refer to herbicides, insecticides, fungicides as well as many others (e.g. nematicides, fumigants, etc.). The demand for increased production has led to an approximate 30-40% increase in the use of pesticides in farming. This trend is predicted to continue to increase substantially in the coming decades (Liu et al., 2015b). Although the use of pesticides has obvious benefits, such as protecting crops and increasing yields, the consequences of its use have widely influenced both the environment and human health (Ecobichon, 2003; Enserink et al., 2013). Considering both the increasing use of pesticide and the rising concerns surrounding its use, the ability to accurately determine and eventually reduce the overall risk of a pesticide - beyond the information on the label - is essential and unfortunately lacking.

The fate of pesticides in the environment can follow different processes depending on a pesticide's properties: uptake by plants, drifting, volatilization, interception, infiltration/leaching, runoff and transport in sediment, adsorption/desorption and decay (Figure 1.1). After application, a pesticide can be taken up by a plant and thus enters the plant's physiological processes. Although part of the pesticide volatilizes into the atmosphere (Burrows et al., 2002) or is assimilated by plants, most of it ultimately reaches the soil and becomes involved in soil physiochemical processes, such as dissolution, adsorption, desorption, and decay (Ahuja et al., 2000; Gavrilescu, 2005; Laitinen et al., 2007). There is a consensus that pesticide fate depends primarily on its pesticide physiochemical characteristics (Báez et al., 2015) as well as the climate conditions (Chen, 2007) which lead to different decay mechanisms, adsorption-desorption behaviour and half-life times in the soil matrix (FOCUS, 2000; Kalam et al., 2004). Additionally, a pesticide can be transported together with surface water and be susceptible to erosion processes, infiltrate and move into deeper soil layers via soil macropores (Styczen et al., 2011a), or leach into groundwater (Vereecken, 2005).

Inappropriate farming practices and overuse of pesticides on cultivated land has resulted in not only on-site pollution but also off-site problems (Damalas, 2009; Enserink et al., 2013; Hao et al., 2014; Yadav et al., 2015). Continuous application of a pesticide can lead to serious degradation of soil (Brunet et al., 2009) as well as affect the quality of surface and groundwater (Geissen et al., 2010; Kalita et al., 2006; Malaguerra et al., 2013; Ongley et al., 2010), drinking water (Chau et al., 2015; Fuscoletti et al., 2015), and even commercially available mineral water and soft drinks (Johnson et al., 2006). Studies have reported that pesticides from agricultural systems, together with surface runoff, contribute more chemical loading to water bodies than pollutants from industrial discharges (Wang et al., 2015a). In some hotspots, especially in high erosion areas, the off-site transport of pesticides has become the main source of pollutants aggravating aquatic ecosystems (Rabalais, 2002; Slaninová et al., 2009; Sun et al., 2012), challenging food security, and threatening human health via the aquatic food chain (Liu et al., 2015a; Perry et al., 2014). Therefore, pesticide in the soil-water system has become a global environmental concern often coupled with the increasing demand for food (Damalas and Eleftherohorinos, 2011; Guo et al., 2014; Rashid et al., 2010; Sinha et al., 2011; Wang et al., 2015a).

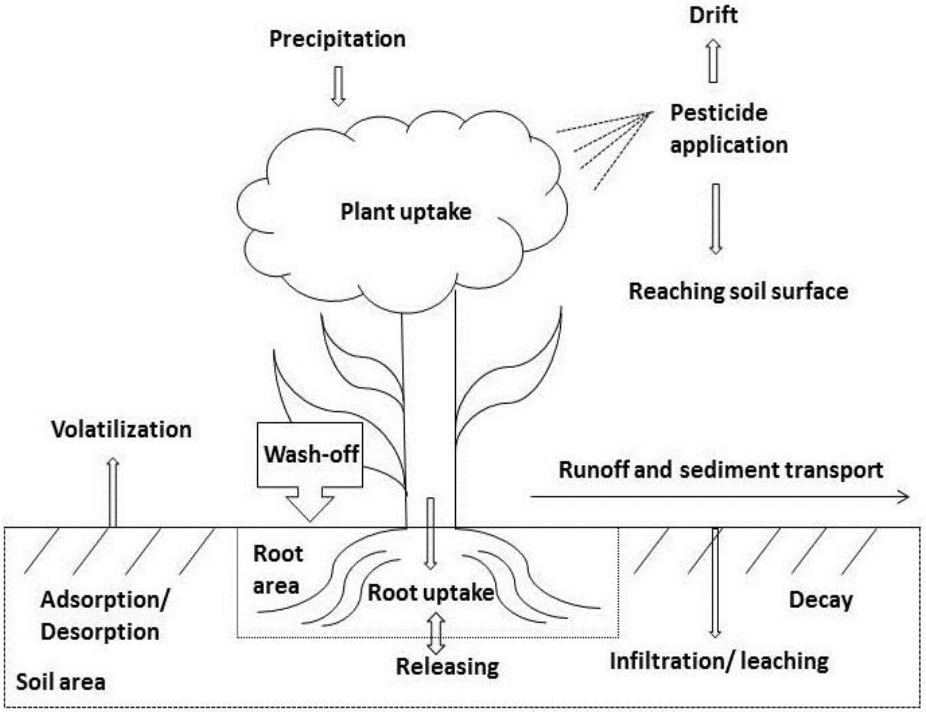

Figure 1.1 *The fate of pesticide after spraying*

Reducing pesticide use is an important way to mitigate the effects of pesticides on the environment. However, the accurate assessment of risks and how to effectively reduce use is a challenge. The pesticide users as well as the related stakeholders who are responsible for pesticide production, safety and use are all participants in this issue

(Pedlowski et al., 2012). Although pesticides are developed and regulated by strict laws to minimize the impact on human health and the environment (FOCUS, 2000; Handford et al., 2015), serious concerns have been raised about health risks resulting from occupational exposure (Damalas and Eleftherohorinos, 2011; Dasgupta et al., 2007; El-Zaemey et al., 2013; Yang et al., 2014b). Occupational exposure to pesticides occurs mainly to agricultural workers in fields and greenhouses (El-Zaemey et al., 2013; Enserink et al., 2013; Hvistendahl, 2013; Karunamoorthi et al., 2012). The lack of knowledge, low education level, and insufficient facilities make it difficult for farmers and agricultural workers to use pesticide properly and safely. This leads to serious poisoning and acute or chronic diseases (Chen et al., 1998; Dasgupta et al., 2007; Eddleston et al., 2002; Hvistendahl, 2013; Recena et al., 2006; Zhou et al., 2011). In addition, overuse or mixing of pesticides increases the risk to both human health and the environment (Pedlowski et al., 2012; Zhang et al., 2015). The adverse effects of pesticides on the environment and human health, depend on multiple factors including the toxicity of the pesticide, dosage applied, application practices, fate of the pesticide in the soil (including its half-life and persistent metabolites), climate conditions after application and people's awareness levels regarding pesticide use (Enserink et al., 2013; Fan et al., 2015; Matthews, 2008). All of these factors make it difficult to fully assess pesticide risk either on human health or on the environment, particularly when the cultivation system, conventional practices and local climate are taken into account (Damalas and Eleftherohorinos, 2011).

China has a long history of cultivation. It also has the world's highest application, exportation, and production of pesticides (Zhang et al., 2011b). The annual application of pesticides in China increased by 120% between 1991 and 2008 (Sun et al., 2012). Every year, roughly 500 to 600 million tons of pesticides are used for crops with an average application dose of about 14.8 kg ha^{-1} (DRSE(NBSC), 2013). The Chinese authorities have implemented a series of policies and regulations to minimize pesticide toxicity and residues in an effort to protect the environment (Valk et al., 2014). Even though some highly toxic, persistent, and bioaccumulative pesticides such as DDT and HCHs have been forbidden in China since 1983, they were previously available for many years (Zhang and Lu, 2007). Consequently, high levels of residues, such as Lindane (γ-HCH) and p, p'-DDT, have been detected in rivers and lakes (FAO, 2013; Grung et al., 2015; Zhang et al., 2011a). With the overall increase in pesticide application, non-point agricultural pollution has become a severe issue in China (Liu and Diamond, 2005; Zhang et al., 2007).

Additionally, soil erosion occurs frequently in China, with approximately 70% of the land suffering from soil erosion especially in Loess Plateau (Zhao et al., 2013). A recently released report shows that soil erosion in the Loess Plateau has decreased significantly since the 1990s when the “Gain for Green Project” strategy was followed (Chen et al., 2015). None the less, the condition of the farmland is not satisfactory in many cases and areas are still subject to soil erosion, the loss ranging from 8 to 49t ha^{-1} a^{-1} under conventional tillage (Guo et al., 2015). Surface runoff and soil erosion related transport of pesticides can have serious off-site effects (Li et al., 2011), however knowledge on this point is scarce. Considering the intense farming, pesticide use and erosion situation in China, and in the loess area in particular, it is important to better understand pesticide fate and its transport properties in order to assess the environmental risks both on-site and off-site (Köhne et al., 2009).

1.2 Environmental fate of glyphosate

1.2.1 Glyphosate and its metabolite AMPA

Herbicide consumption worldwide has increased rapidly, from 20% of all pesticide use in 1960 to 48% of pesticide use in 2005, and this trend is undoubtedly continuing (Zhang et al., 2011b). Since paraquat was banned in 2012, glyphosate or glyphosate-based herbicides have become the most widely applied herbicide worldwide, especially on genetically modified crops (Brookes and Barfoot, 2015). With the intensive use of these kinds of herbicides, the occurrence of glyphosate in soil, sediment and water bodies, as well as risks to human health, has been frequently reported (Majewski et al., 2014; Ruiz-Toledo et al., 2014; Samsel and Seneff, 2015). Glyphosate (N-(phosphonomethyl)glycine; $C_3H_8NO_5P$), a highly efficient broad-spectrum and non-selective herbicide, has been widely used in agriculture, horticulture, parks, and domestic gardens (Wojtaszek et al., 2004), especially on glyphosate-tolerant crops (Beckie and Hall, 2014; Liphadzi et al., 2005). It was first marketed in 1974 under the name Roundup by Monsanto, USA. Its use has increased rapidly with the commercial introduction of genetically modified corn, soybeans, and cotton in 1996 (Brookes and Barfoot, 2015). With the expiration of Monsanto’s patent in 2000, many other companies began producing relatively inexpensive generic equivalents (Livingston et al., 2015).

The decay of glyphosate in soil mainly depends on microorganisms (Liphadzi et al., 2005; Schroll et al., 2006). There are two common abundant pathways of enzymatic glyphosate breakdown in soil: the oxidative cleavage of the C-N bond and the formation of environmentally stable AMPA which can either be excreted or undergo further metabolism, and the breaking of the C-P bond to generate sarcosine (Borggaard and Gimsing, 2008; Kishore and Jacob, 1987; Sviridov et al., 2012). AMPA is considered to be the main metabolite product of glyphosate even though this remains to be clarified (Borggaard and Gimsing, 2008).

1.2.2 Glyphosate and AMPA fate in the soil-water environment

As a systemic herbicide, the behaviour of glyphosate varies due to its component groups and physiochemical reactions in environmental systems. Concerning the physical properties, there is very little volatilization of glyphosate into air, however, the water solubility is 10.1 g L^{-1} at 20°C (WHO, 2005) indicates the potential risks for aquatic life and human health (Samsel and Seneff, 2015). 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; Gimsing et al., 2004b; Sheals et al., 2002b). As an organophosphate herbicide, glyphosate strongly 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., 2002b; Sprankle et al., 1975). Hence, these properties of glyphosate need to be taken into account in order to trace its fate and translocation, especially its distribution in farming systems. Glyphosate is strongly adsorbed onto soil particles and the observed K_{oc} values for glyphosate range from 9 to 60000 L kg^{-1} depending on the surface characteristics of the soil matrix (Candela et al., 2007; Giesy et al., 2000a; Mamy and Barriuso, 2007). The linear distribution coefficient of glyphosate (K_d) varies from 1.2 to 2751 L kg^{-1} (Cheah et al., 1997; Gjettermann et al., 2009; Lanctot et al., 2013; Sorensen et al., 2006; Strange-Hansen et al., 2004; Wang et al., 2005b). Glyphosate adsorption onto soil particles is usually described by the Freundlich sorption isotherm (Nomura and Hilton, 1977; Sprankle et al., 1975). With two important parameters 1/n and K_f, the Freundlich exponent and the Freundlich distribution coefficient, respectively, numerous studies have shown that large variations are observed in 1/n values, ranging from 0.46 to 1.16, while the values of K_f range from 0.6 to 5.0×10^5 (Vereecken, 2005). Mechanisms controlled by soil properties, such as organic matter, pH, clay fraction, and irons quantities, have been discussed as factors to explain the variations of glyphosate adsorption (Dollinger et al., 2015; Ololade et al., 2014). Glyphosate's primary metabolite, AMPA, is also strongly adsorbed onto soil but understanding of the parameters related to AMPA's adsorption/desorption are still limited (Simonsen et al., 2008).

The half-life of a chemical is an important parameter for assessing environmental threats. The half-life of glyphosate ranges from 1.2 to 197 d in soil (Al-Rajab and Hakami, 2014; Bergström et al., 2011; Mamy and Barriuso, 2007; Rueppel et al., 1977) and from 1.3 to 4.8 d in water (Degenhardt et al., 2012). AMPA has a lower water solubility (5.8 g L^{-1} at 25 ◦C) (Grunewald et al., 2001) and a longer half-life ranging from 9 to 240 d in soil (Al-Rajab et al., 2008; Al-Rajab and Schiavon, 2010; Bergström et al., 2011; Borggaard and Gimsing, 2008; De Jonge et al., 2000; Giesy et al., 2000b; Mamy et al., 2010) and from 2.07 and 15.5 d in water (Levine et al., 2015). Studies show that the variation in glyphosate and AMPA half-life times strongly depends on soil properties and climatic conditions (Al-Rajab and Schiavon, 2010; Bergström et al., 2011; Zhao et al., 2009). Repeated applications of glyphosate have increased its soil half-life time (Lancaster et al., 2009) leading to the high occurrence of both it and AMPA being detected in the environment frequently (Battaglin et al., 2014; Ruiz-Toledo et al., 2014).

1.2.3 Off-site risk of glyphosate application and AMPA formation

The intensive use and widespread application of glyphosate indicate a potential for this pesticide to reach surface water as a result of spray drift, run off and particulate transport by soil erosion (Rashid et al., 2010). Todorovic et al. (2014) showed that approximately 47% of applied glyphosate was transported in the runoff associated with erosion in farmland, and Degenhardt et al. (2012) reported that 67% of the glyphosate (AMPA) added to the system was detected in wetland sediment within 77 d after application as a result of the off-site effect. This indicates that glyphosate is mainly transported by sediment which is referred to as particle-facilitated transport (Rügner et al., 2014; VandeVoort et al., 2013).

The high occurrence of glyphosate and AMPA found off-site implies that there are high risks from this material for the environment and human health. With long-term glyphosate-based pesticide application, aquatic organisms and earthworms are seriously affected (Yadav et al., 2013; Zaller et al., 2014). Furthermore, some studies reported that glyphosate is related to non-Hodgkin's lymphoma (De Roos et al., 2003). Currently, the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) has issued a summary of the final evaluations of glyphosate that classifies it as "Probably Carcinogenic to Humans" (Fritschi et al., 2015; Samsel and Seneff, 2015). The ability to fully assess the risk of glyphosate and AMPA is thus required to accurately evaluate their threats and to determine the specifics of glyphosate application and related pesticide management (Todorovic et al., 2014; Zablotowicz et al., 2009).

1.3 Prediction of off-site pesticide risk

To assess the risks of pesticides in the environment, multiple approaches based on both field observations and simulations at different scales have been reported (Zhang et al., 2012). Concerning the risks related to the off-site transport of pesticide, several models have been developed. Physical or mathematical models are often proposed to simulate leaching via soil macropore (Styczen et al., 2011a), such as the one-dimensional models MACRO (Jarvis et al., 1994) and PRZM_GW (Carsel et al., 1985) which have been recommended for distinct EU situations (Beltman et al., 2008; FOCUS, 2000). Other models such as LEACHM (Hutson et al., 1989), PLM (Nicholls et al., 2000), PEARL (Leistra et al., 2001), and GeoPEARL (Tiktak et al., 2002) were developed either based on principles of chemical dispersion or on advanced technology, e.g. geographic information system. Surface runoff is another important mechanism for pesticide displacement, especially in highly erosive areas (Ulrich et al., 2013). During intensive rainfall, pesticides may move both as a solute in runoff water and attached to eroded soil particles (Majewski et al., 2014). This displacement may adversely affect ponds, lakes, rivers, and aquatic ecosystems in general (Blann et al., 2009). To simulate pesticide transport in surface water, several models have been developed such as ARM (Donigian and Davis, 1978), CREAMS (Knisel, 1980), ANSWERS (Dillaha III and Beasley, 1983), AGNPS (Young et al., 1986), RZWQM (Ahuja et al., 2000), GeoPEARL(Tiktak et al., 2002), and PeLM (Chen et al., 2004). These models for pesticide risk assessment mainly focus on the pesticide dissolution fraction while the adsorbed pesticide transported with particulate matter is not simulated (Majewski et al., 2014). As shown in Figure 1.1, pesticide in soil is also involved in the degradation process that leads the dynamics of pesticide residues on-site and off-site. Therefore, it is high time to develop a model which can combine pesticide decay properties with soil erosion processes to better predict off-site pesticide risks, especially the risk resulting from particle-facilitated transport.

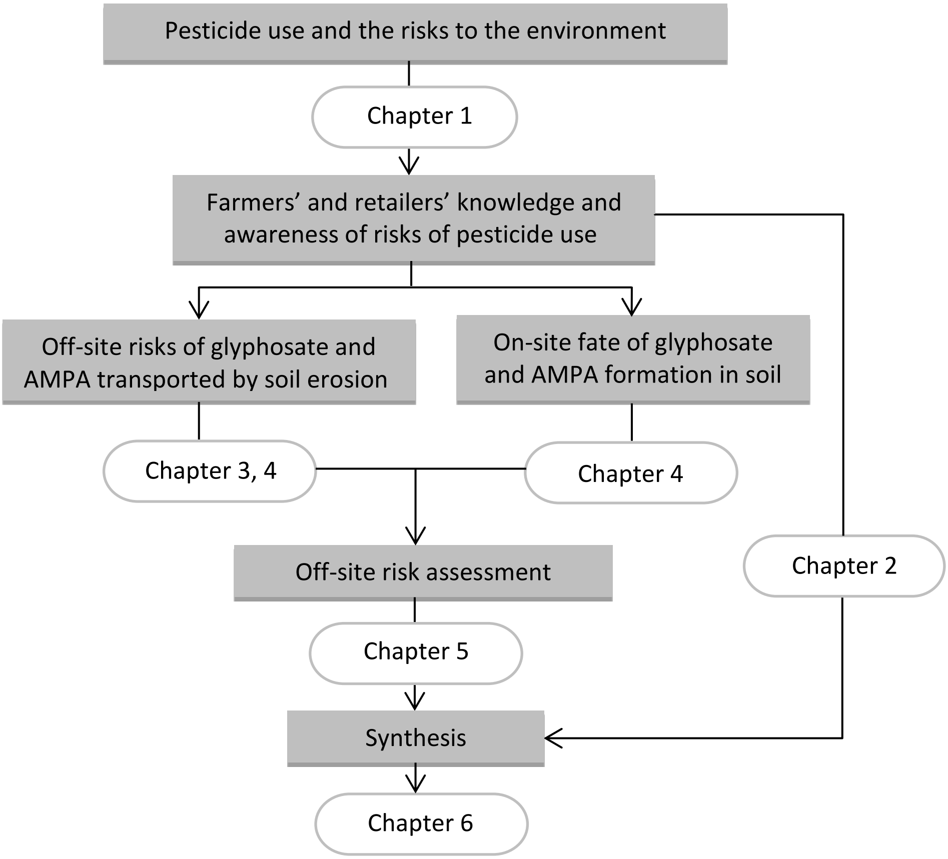

Figure 1.2 *Outline of the thesis*

1.4 Objectives

This PhD study aims to further the science of pesticide risk assessment by increasing the understanding of the fate of glyphosate and AMPA while also assessing their risks related to soil erosion in Chinese loess soil. The outline of the thesis can be seen in Figure 1.2. The research objectives are as follows:

1 Assessment of farmers' and retailers' knowledge and awareness of pesticide use in the Wei River catchment

2 Investigation of off-site risks of glyphosate and AMPA transported by runoff and erosion in Chinese loess soil
3 Investigation of the on-site fate of glyphosate and AMPA formation in Chinese loess soil
4 Off-site risk assessment of particle-facilitated pesticide transport related to erosion

1.5 Outline of this thesis

This thesis comprises 6 chapters. Chapter 1 contains this general introduction to pesticide use and risk assessment, an introduction to the herbicide glyphosate, and the outline of the thesis.

Chapter 2 describes the attitude and awareness of farmers and retailors regarding pesticide use based on face-to-face interviews. The most relevant factors for the safe use of pesticides were analysed. Strategies to reduce pesticide use for both sellers and end users are recommended.

Chapter 3 presents the results of research on the transport of glyphosate by erosion under simulation of short-term rainfall (1 h). The distribution of glyphosate and AMPA in runoff, sediment, and soil layers were quantified.

Chapter 4 studies the characteristics of glyphosate decay and AMPA formation in Chinese loess soil under field conditions. Their transport related to soil erosion is studied.

Chapter 5 describes a newly developed parsimonious integrative model for pesticide displacement by runoff and soil erosion that explicitly accounts for water infiltration, erosion and runoff, and pesticide transport and degradation in soil.

Chapter 6 summarizes the major conclusions of this research and discusses their implications. Findings from this thesis have a broader application than just glyphosate behaviour in Chinese loess soil. Recommendations for reducing pesticide risk related to erosion are proposed.

Chapters 2, 3, 4, 5, have been published in highly ranked peer reviewed journals. All key methods, data and results are presented in those chapters. The information for these publications can be download and cited as shown at the beginning of each chapter.

1.6 Study area

The study area is located in the Wei River catchment, in northwest China (Figure 1.3). The Wei River catchment, with 84 counties and around 33 million inhabitants, is north-western China's major region for agriculture, industry and commerce. It is located in the continental monsoon climate zone, with annual rainfall ranging from 450 to 700 mm, and annual evaporation ranging from 1,000 to 2,000 mm. The main river in this basin, the Wei River, is the largest tributary of China's Yellow River. It originates in Gansu Province, and passes through the central Shaanxi plain. The river is 818 km long and covers an area of 135,000 km^2. It is a major source of water, including drinking water, and a key to industrial production and agricultural activities in the central Shaanxi plain (Webber et al., 2008).

We selected the villages of Chencang and Qianyang to conduct our surveys with farmers and retailers' regarding their perspectives on pesticide use as well as their pesticide practices. These two areas were chosen because they have different landscapes and cultivation systems. They are especially different in terms of erosion and crop production. Field monitoring and simulation experiments were carried out at the Linghou field station and in the simulation rain hall at the Institute of Soil and Water Conservation respectively. Both of these facilities are in the District of Yangling where agriculture activities are intensive and soil erosion occurs frequently.

Yangling lies about halfway along the Wei River, at 107°59'- 108°09' E and 34°14'-34°24'N and has an elevation of 418.0~540.1m. The climate is semi-humid and the annual average temperate is 12.9℃, with 42℃ as the maximum and -19.4℃ as the minimum. Average precipitation per year is about 637.6mm and there is an obvious rainy season which lasts for 4 months (from July to October) and delivers 60% of the rainfall for the whole year. The terrain is quite variable with different levels of terraces throughout the whole region. The soil type is Anthrosol which belongs to the loess soil group. In addition, farm activities are intensive in the Yangling region and most farmers adopt traditional practices for crop cultivation.

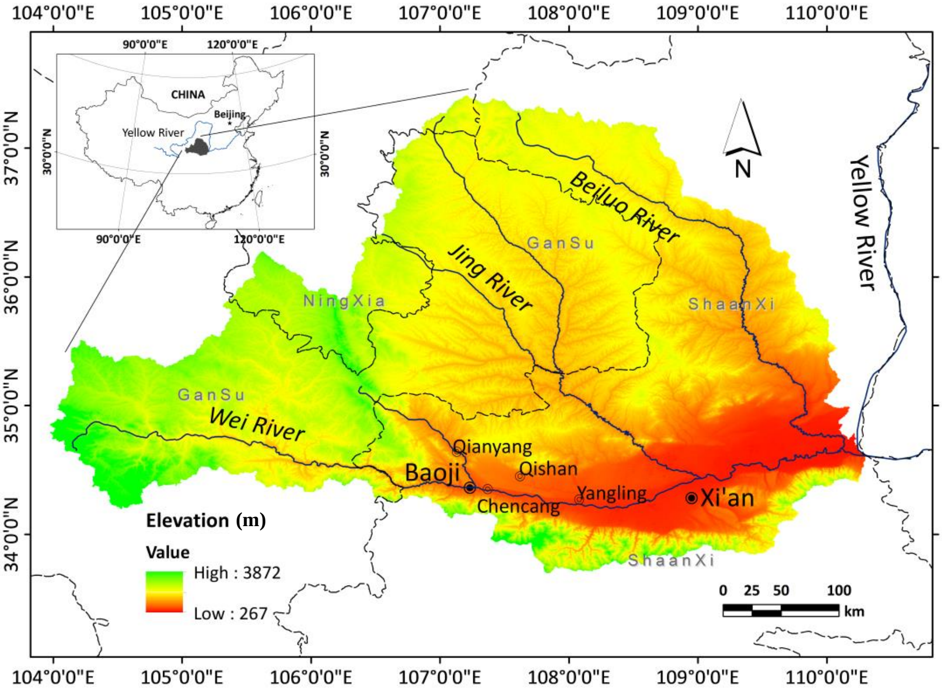

Figure 1.3 *Experiment sites in Wei River catchment of China*

2 Farmer and retailer knowledge and awareness of the risks from pesticide use: a case study in the Wei River catchment, China

Monitoring the educational level of farmers and retailers on pesticide use would be useful to assess the appropriateness of information for reducing or/and avoiding the risks from pesticides in rural regions. The levels of knowledge and awareness of the dangers to the environment and human health were investigated by questionnaires for farmers (209) and retailers (20) in two rural regions (Qianyang County (S1) and Chencang County (S2)) of the Wei River catchment in China where the modes of farming and the state of erosion are very different. The results showed that farmers learned the use and dangers of pesticides mainly by oral communication (p<0.01). Protective measures were inadequate; 65% (S1) and 55% (S2) of farmers never used any protective measures during spraying (p<0.05). Washing hands (>70%) was the most common mode of personal hygiene, relative to wearing masks, showering, and changing clothes, but no significant differences were observed between the selected regions. Most pesticide wastes were dumped directly onto the land or into water, suggesting that educational measures should be taken to address the potential risks from the residues in the wastes. Over 85% of farmers (S1 and S2) claimed to use illegal pesticides, but the reasons for their use varied (p<0.01). Retailers were well-informed and highly conscious of their responsibility for the safe use of pesticides, especially in S2 (p<0.01). A canonical correspondence analysis indicated that educational level and age differed between the two regions and contributed greatly to the risks from pesticide use (p<0.01). Educational programmes targeted to age groups, proper disposal of pesticide waste, and sufficient supervision from authorities should consequently be considered for improving the levels of knowledge and awareness of the dangers of pesticides to human health and environmental pollution in the Wei River catchment, China.

Based on:
Yang X., Wang F., Meng L., Zhang W., Fan L., Geissen V. Ritsema C.J.
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2.1 Introduction

Intensively used pesticides, despite their ability to protect crops, threaten the environment and human health (Damalas, 2009; Damalas et al., 2008; Hvistendahl, 2013; Peshin and Dhawan, 2009; Verger and Boobis, 2013). These “poisons by design” are prevalent and serious occupational hazards faced by agricultural workers and farmers (Gomes et al., 1999; Gunnell and Eddleston, 2003; Hogstedt et al., 1997; Hvistendahl, 2013; Ibitayo, 2006; Yassin et al., 2002). The high levels of occupational exposure to pesticides are correlated with low educational levels, which would preclude the ability of farmers to follow the hazard warnings developed by the chemical industries and agencies (Ibitayo, 2006; Ngowi et al., 2007a; Ngowi et al., 2007b; Recena and Caldas, 2008). Tragedies such as acute and chronic intoxication, and in some extreme cases, suicide, have frequently been reported, especially in rural regions (Cui, 2009; Gunnell and Eddleston, 2003; Hvistendahl, 2013; Karunamoorthi et al., 2011; Karunamoorthi et al., 2012; Koh and Jeyaratnam, 1996; Konradsen et al., 2003; Kumar et al., 2012; Phillips et al., 2002; Yassin et al., 2002; Zhou et al., 2011). The lack of a legislative framework regulating the use of pesticides also contributes to the high incidence of poisoning in developing countries (Chen et al., 1998; Hvistendahl, 2013; Salameh, 2004; Yassin et al., 2002). Accountability system, from pesticide registration to supervision mechanism, taking China for instance, is unequipped (Chen et al., 1998; Zhang and Lu, 2007) which leads some big challenges to trace pesticides in market, environmental system and its consequences for human being via food chain(Enserink et al., 2013; Peshin and Dhawan, 2009; Verger and Boobis, 2013). Taking into account the interactions among mixed pesticides, it also increases the risk to human health and the environment (Pedlowski et al., 2012). Poverty, inadequate sanitation, and the standards of medical care are also obstacles to the safe use of pesticides. Those aware of the risks, however, may still misuse pesticides to avoid a lower crop production associated with a significant lower pesticide use (Enserink et al., 2013; Tucker and Napier, 2001). No awareness of alternative systems of production appears to lead to the idea that the use of agrochemicals is unavoidable.

China has a long history of cultivation and has the highest application, exportation, and production of pesticides (Zhang et al., 2011b). The annual mean rate of pesticide application in China is 14.8 kg ha^{-1} (DRSE(NBSC), 2013) but the application rate is likely higher in hotspots. Some highly toxic, persistent, and bioaccumulative pesticides such as the chlorinated pesticides have been completely banned since 1983, but some of these are still commercially available (Zhang and Lu, 2007), and high levels of residues are still detected in soils and water (FAO, 2013; Zhang et al., 2011a). Not all regulations and provisions for pesticide management are respected and accepted in rural regions (Li et al., 2002; Zhang et al., 2005). The Wei River catchment is an important region of agricultural development, and the Wei River contributes strongly to the local economy and society. Due to severe anthropogenic activities, however, the water quality in this river has been degraded by over 85% to class IV of the national standards (GHZB 1-1999), indicating that the water cannot be used for either drinking or irrigation (Guo, 2011; Li et al., 2011; Liu et al., 2007; Zhang and Lu, 2007). Many measures and policies, such as the Program of Integrated Management of Pollution in the Wei River [G2005-99], have addressed the direct discharge of pollutants into the Wei River, however, the quality of the water is still deteriorating (Guo, 2011). Li et al. (2011) suggested that agrochemicals (fertilizers) were a source of pollution contributing to the high concentrations of nitrogen and phosphorous in the Wei River. The levels of knowledge and awareness of the stakeholders, especially farmers and retailers, of the hazards of pesticides should be taken into account to enhance the integrated management of agricultural pollution and agrochemical supervision in rural regions. Such studies are unfortunately limited in China (Huang et al., 2003; Huang et al., 2000; Zhang and Lu, 2007) and the poisoning and suicide case from pesticides are reported frequently (Cui, 2009; Zhou et al., 2011). As end users and distributors, farmers and retailers of pesticides are directly exposed to pesticides, and their behaviour for the safe use of pesticides play an important role in reducing point and non-point sources of pollution, hazards, and acute or chronic intoxication to pesticides in agricultural regions. The levels of knowledge and risk awareness and the practices of farmers and retailers are essential elements for increasing the efficiency of devising to protect these stakeholders. The objectives of this study were thus (1) to determine the levels of knowledge and awareness and the practices of farmers and retailers of pesticide use in regions with different modes of farming and terrains, (2) to evaluate the related risks to the environment and human health and to analyse the most relevant factors for the security of pesticide use, and (3) to recommend programmes for reducing pollution and the risks from pesticide use based on the comparative results of a survey in two regions of the Wei River catchment in China.

2.2 Materials and methods

2.2.1 Study site

This study was conducted in two typical rural regions in the middle region of the Wei River catchment (107°04′-107°59′ E and 34°31′-34°74′ N) (Figure 1). One region (S1) is located in

Qianyang County along the Qian River, a branch of the Wei River. S1 has an area of 2290 ha and has approximately 50000 inhabitants scattered in hilly regions where arable land is terraced and fruit trees are commonly grown. Wheat and maize are also cultivated and irrigated on the limited flat land. The steep slopes of the land and the concentrated rainfall (June to September) have led to serious losses of soil and nutrients and to the degradation of the land. Most of the younger farmers (<40 years of age) also work outside this area due to the difficulty in procuring an adequate income. The other selected region (S2) is located at the junction of the Chencang and Qishan County on the north shore of the Wei River. S2 has an area of 1560 ha and approximately 45 000 inhabitants. The farmland is flat, and the irrigation system is well developed. S2 has a convenient transportation system and good farming conditions. Mushrooms and vegetables are grown in small-scale greenhouses, and traditional crops such as wheat and maize are intensively cultivated. Both study sites are far from large urban areas and are thus not strictly supervised by authorities. The practices of agrochemical use are thus determined by the level of knowledge of the local farmers.

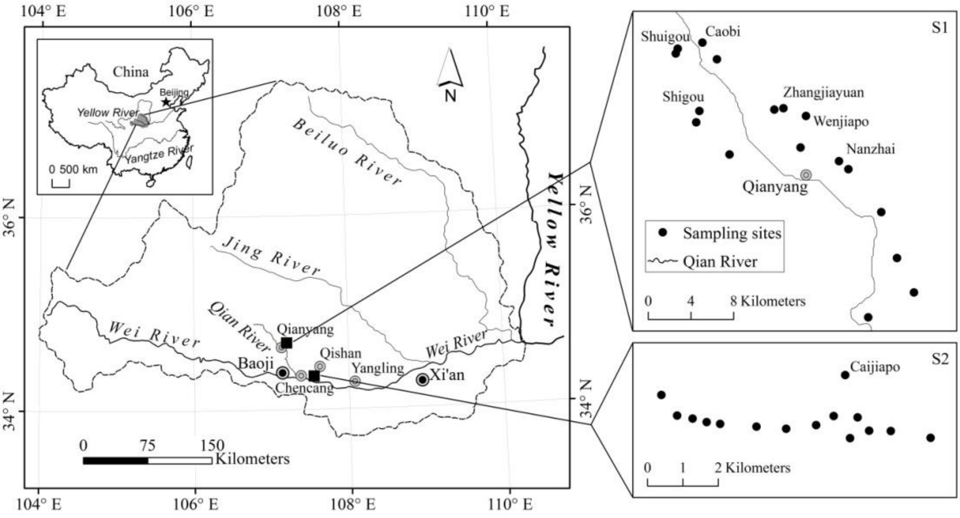


Figure 2.1 *The geographical location of selected study areas: Qianyang (S1) and Chencang (S2)*

2.2.2 Survey

A questionnaire was designed to survey the farmers in the selected regions. The local pesticide store was the only direct source of pesticides for the farmers, so a related questionnaire was designed to survey the levels of knowledge of pesticides and the attitudes and practices of the retailers. The questionnaires focused on: 1) basic information about the interviewee, such as gender, age, educational level, and their farming practices (crop types and yields, agrochemical products used, expenditures, and income); 2) the practices of pesticide application and the pesticides commonly used; and 3) the level of awareness of the dangers of pesticides (Table 2.1a-c). To ensure the efficient and economical application of the questionnaires, we first contacted the local leaders or deputies in the villages and talked with them an half of day to obtain basic information, e.g. the number of families and the average areas of the farms. Farmers were completely randomly selected and they were entirely voluntary. The heads of the selected families, i.e. those who purchased and applied the agrochemical products, were interviewed face-to face. The purpose of the survey was clearly explained to minimise the apprehension of the participants or potential bias, and all interviewees remained anonymous. All retailers from the pesticide stores in the two study areas were interviewed as the same way like farmer. The interview lasted around an hour and a economical compensation gift (towels, soaps or detergent) cost 1.5 $ was supplied to each participant.

Table 2.1a *The questionnaire on farmers' knowledge, awareness and the risk of pesticides*

Questions
Part 1 Basic information
1. Gender /Age/Education level
2. Family members, farmland area, crop types, income from farming and expenditure on pesticides
3. Pesticides names, types and dose for crops
Part 2 Pesticide practice
1. How do you know pesticides?
2. Where do you store pesticides?
3. How do you apply pesticides?
4. Which kinds of protection do you use when you apply pesticides?
5. How do you dispose container of pesticides?
6. Which kinds of measurements you take after applying pesticides?
7. Do you know some pesticides have already forbidden recent years? If yes, please note them.
8. Do you know the reasons why pesticides were forbidden?

2.2.3 Data analysis

The raw data from the questionnaires were reviewed after the interviews. The answers to each question were then coded and entered into Excel. The statistical analyses, using SPSS 20.0, were based on the relative proportions in each region. Chi-square tests ($p<0.05$)

were used to compare the differences between the two regions. We used Kruskal-Wallis tests for quantitative variables with nonhomogeneous variances or nonnormal distributions and analyses of variance for quantitative variables with normal distributions and homogeneous variances. A canonical correspondence analysis using Canoco 5 was selected to determine the relationship between the backgrounds of the interviewees and their levels of awareness of the dangers of pesticides to the environment and human health.

Table 2.1b *The questionnaire on retailers' knowledge, awareness and the risk of pesticides*

Questions
Part 1 Basic information
1.Gender /Age/Education level
2. Working years and permission certificate
3.Commonly used list of pesticides information
Part 2 Pesticide selling
1. Do you give suggestions /guidelines when farmers buy pesticides?
2. Do you think where is suitable place for pesticides storage?
3. Do you think protective measurements are necessary?
4. How to handle container of pesticides?
5. Do you know some pesticides have been forbidden in recent years? If yes, please note them.
6. Do you know the reasons why some pesticides were forbidden?

Table 2.1c *The questionnaire of interviewees' cognition of the awareness and risk of pesticides on environment and human health*

Questions
1. Do you know pesticides residues?
2. Do you think pesticides are harmful for human health?
3. Do you know environment can be impacted by pesticides?
4. Do you think water pollution is related with pesticide application?
5. Do you know the relationship between pesticides and illness?
6.Do you know how to handle the risk of pesticides? If yes, please note.

2.3 Results

2.3.1 Social and demographic characteristics

We interviewed 209 farmers and 20 retailers from 23 villages in these two study areas (Table 2.2). S1 had more farmers (118) than did S2 (91), but each area had 10 retailers. The majority of individuals were males, 68.8 and 57.4% in S1 and S2, respectively. More than half of the participants (66) in S1 were over 50 years of age, and 46 were 40-50 years old, together comprising 86.8% of the interviewees. These two age classes, however, were evenly distributed near 25.0% in S2, with a standard deviation of 6.3% in each age class. Educational levels were significantly different between the two regions. In S1, 35.9% of the respondents were illiterate, a proportion similar to that of people educated at the primary-school level. High-school education was extremely limited, with only 3.1% of the people in S1 having graduated. The majority of the respondents in S2, however, were educated in middle and high schools, comprising 58.4% of the interviewees, and only 20% of the respondents were illiterate.

Table 2.2 *Background of interviewee in two study regions*

Category	Variables	Qianyang		Chencang	
		No.	%	No.	%
Respondent		128	100	101	100
Occupation	Farmer	118	92.2	91	90.1
	Retailer	10	7.8	10	9.9
Gender	Male	88	68.8	58	57.4
	Female	40	31.3	43	42.6
Age	≤30	2	1.6	19	18.8
	30-40	15	11.7	23	22.8
	40-50	45	35.2	25	24.8
	≥ 50	66	51.6	34	33.7
Education level	High school	4	3.1	26	25.7
	Middle school	34	26.6	33	32.7
	Primary school	44	34.4	19	18.8
	Illiteracy	46	35.9	23	22.8

2.3.2 Farmer income and expenditures for agrochemicals

Socioeconomic variables, including number of people and farm area per family, total income from cultivation, and total expenditure on agrochemical products, differed significantly (Table 2.3) between regions. According to the survey, more farmland was owned and available for farmers in S1 (0.05-0.1 ha per farmer) than in S2 (0.03-0.05 ha per farmer). Interestingly, the incomes were quite different between the regions. Families in S2 had a mean income of 10 072.4 \$ ha^{-1} y^{-1} from cultivating vegetables (broccoli, leeks, Chinese cabbage and celery, pepper, eggplant, cucumber, tomato, summer squash, garlic, potato, onion, carrot, mushroom, and other cash crops (watermelon and sweet melon), compared to a mean income from agriculture in S1 of 1962.4 \$ ha^{-1} y^{-1} where only crops (maize and wheat) and fruit trees (apple, plum, nuts and pear trees) are planted in limited irrigated land. This significant difference was attributed to the structure of the agriculture, the availability of irrigation, and the long-term management of cultivation. Concerning the intensities of pesticide use in pre-harvest (vegetable > 5 times; crops≤ 2 times, fruit trees ≤3 times), the expenditures on agrochemical products (fertilizers and pesticides) were similar in both regions, but the proportions for pesticides to the total expenditure were quite different, 0.7 and 2.7% in S1 and S2, respectively.

Table 2.3 *Total income, expenditure and cost for pesticide form agricultural cultivation per family in two study regions**

Region	Number of People per household	Farmland (ha farmer^{-1})	Total income (\$ ha^{-1} a^{-1})	Total expenditure (\$ ha^{-1} a^{-1})	Pesticides cost (\$ ha^{-1} a^{-1})
Qianyang	5~7	0.05~0.10	1962.4	364.9 (18.6%)	14.3 (0.7%)
Chencang	3~6	0.03~0.05	10072.4	1855.2 (18.4%)	265.1 (2.7%)

* 1\$=6 RMB

2.3.3 Farmer knowledge of and behaviour towards pesticides

We analysed the level of the knowledge of pesticides of the farmers, including information sources, practices, and protective management (Table 2.4). Most farmers learned about pesticides by oral communication with retailers or other farmers, and 5-fold fewer farmers in S1 relative to S2 (p<0.01) learned about pesticides via media, e.g. television, the internet, newspapers, or books. Over 40% of the farmers in these two regions claimed that they seldom store pesticides at home but buy them when needed. In S1, 31.4% of the farmers admitted that they haphazardly stored pesticides, and only 22.9% of the farmers declared storing pesticides in specific storerooms. This latter proportion was similar to that in S2. Nearly half of the farmers in S1 admitted that they trusted their own experience of application rather than following the specifications on the labels of pesticide containers. The frequencies were significantly different in S2: 47.3% of the farmers obeyed the suggestions of the retailer, 30.8% followed the specifications and only 22.9% of farmers use pesticides by their own experience (p<0.05).

Protective measures during and after pesticide application are considered effective means of reducing the risks to farmers. Most farmers, 65.3 and 54.9% in S1 and S2, respectively, stated that they never took any protective precautions during pesticide application because of the good quality of a lever-operated knapsack sprayer. In S1, 26.3% of the farmers used waterproof clothes, similar to the proportion in S2 (29.7%). Few farmers used masks and gloves, especially in S1. A large proportion said that they washed their hands immediately after spraying pesticides (>70%). In S2, 45.1 and 17.6% of the farmers changed their clothes and showered, respectively, but only 28.8 and 8.5%, respectively, of the farmers in S1 took such precautions to avoid the risk of exposure to pesticides. Approximately 20% of all farmers, however, responded that they took no precautions after applying pesticides. A large proportion of the farmers, 84.7 and 79.1% in S1 and S2, respectively, discarded the empty containers near the fields where they prepared the pesticides. The disposal of containers as garbage or burning or burying containers in fields were also reported, but the proportions of these methods of disposal were less than 20%.

The majority of farmers in both regions reported that they knew some kinds of pesticides had already been banned, such as DDT, hexachlorocyclohexanes, parathion, demeton, and thimet, which are all highly toxic and persistent pollutants. A lower proportion paid no attention to such bans, but the proportion was nearly 3-fold higher in S1 than in S2 (p<0.05). A large proportion in S1 (>90%) did not know why these pesticides had been banned, compared to only 1.1% of the farmers in S2. The farmers in S2 believed that commercial unavailability (92.3%), the high toxicity of the pesticide (68.1%), and national control were the critical reasons for the bans, but few of the farmers interviewed in S1 knew of these reasons (p<0.01).

Table 2.4 *Farmers' knowledge and behaviours with respect to pesticide*

Questions	Variables	Qianyang (N= 118)		Chencang (N= 91)	
		No.	%	No.	%
How you do you know pesticides (including new products)?					
χ^2= 14.1**	Retailers	69	58.5	44	48.4
	Other farmers	44	37.3	27	29.7
	TV/Internet/papers/books	5	4.2	20	22.0
Where do you store pesticides?					
χ^2=1.3	Specific storeroom	27	22.9	27	29.7
	Random	37	31.4	25	27.5
	Purchase when used	54	45.8	39	42.9
How do you apply pesticides?					
χ^2=18.6**	Follow specifications	15	12.7	28	30.8
	By experience	58	49.2	20	22.0
	By retailer	45	38.1	43	47.3
Which kinds of protection do you use when you apply pesticides?					
	Mask or respirator	10	8.5	14	15.4
χ^2=8.5*	Water-off clothes	31	26.3	27	29.7
	Wear gloves	7	5.9	16	17.6
	No protection	77	65.3	50	54.9
How do you dispose container of pesticides?					
χ^2=1.0	Drop it directly	100	84.7	72	79.1
	Throw it to garbage	16	13.6	17	18.7
	Burning/burying	2	1.7	2	2.2
Which kinds of measurement you take after applying pesticides?					
χ^2=5.3	Wash hands	90	76.3	66	72.5
	Showering	10	8.5	16	17.6
	Changing cloths	34	28.8	41	45.1
	Never mind	20	16.9	19	20.9
Do you know some pesticides have been forbidden in recent years? If yes, please note them.					
χ^2=6.1*	Yes	102	86.4	87	95.6
	No	16	13.7	4	4.4
Reasons about forbidden pesticides					
χ^2=272.3**	Forbidden by nation	1	0.8	46	50.5
	Stop to sell	4	3.4	84	92.3
	High toxic	5	4.2	62	68.1
	Have no idea	108	91.5	1	1.1

Significant difference between the study regions: * $p<0.05$; ** $p<0.01$

2.3.4 The perception of store owners of the safe use of pesticides

The store owners knew more about pesticide use than the farmers did (*p*<0.01) (Table 2.5). Nearly all the retailers in the two regions emphasised that they provided suggestions for the use of the pesticides they sold. They claimed, especially in S2, that protective measures should be taken before and after use and that new and previously purchased pesticides should be stored in storerooms away from children, water, and food. Most retailers in S2 suggested that empty pesticide containers should be recycled and buried (including burned), accounting for, 90% and 80% of interviewed retailers, respectively. Only 70% of the retailers in S1 recommended burying or burning the containers, and 30% suggested disposing of them as garbage (*p*<0.01). All retailers in S2 admitted that national and other supervisory authorities play dominant roles in their decision to not sell banned pesticides, with toxicity being another important reason. In S1, 60% of the retailers agreed that national controls were important, and half of them thought halted production was also an important reason for the banning or unavailability of pesticides, lower than the proportion in S2 (*p*<0.01).

Table 2.5 *Retailers' knowledge and behaviours with respect to pesticides*

Questions	Variables	Qianyang (N=10)		Chencang (N=10)	
		No.	%	No.	%
Whether you give suggestions/guides when farmers buy pesticides?					
χ^2=10.5**	Yes	9	90	10	100
	No	1	10	0	0
Do you think protective measurements are necessary for pesticides use?					
χ^2=12.5**	Necessary	7	70	9	90
	Never mind	3	30	1	10
Where is suitable place to store pesticides?					
χ^2=22.2**	Storeroom	8	80	10	100
	Never mind	2	20	0	0
How to handle the container of pesticides?					
χ^2=84.7**	Drop directly	3	30	1	10
	Bury/burning	7	70	8	80
	Recycling	0	0	9	90
Reasons about forbidden/unavailable pesticides					
χ^2=46.1**	Nation	6	60	10	100
	Stop to produce	5	50	2	20
	High toxic	2	20	8	80

Significant difference between the study regions: ** *p*<0.01

***Table 2.6** The list of pesticide used in study area*

Registered name[a]	Commercial name[b]	Active ingredient	Type
Carbendazim	Kebaiwei	80% Carbendazim	Fungicide
Cymoxanil	Shuangniaoqin	12% Cymoxanil 38% Propineb	Fungicide
Mancozeb	Daisenmengxin	80% Mancozeb	Fungicide
Metalaxyl-propamocab	Jiashuanglin	15% Metalaxyl 10% Propamocab	Fungicide
Thiophanate	Topsin-M	70% Thiophanate-methyl	Fungicide
Triadimefon	Sancuotong	15% Triadimefon	Fungicide
Zineb	Daisenxin	80% Zineb	Fungicide
Carfentrazone	Zuocaotong	14% Tribenuron-methyl 22% carfentrazone	Herbicide
Butylate	Dingcaodi	2,4-D butylate	Herbicide
Glyphosate	Caoganlin	41% Glyphosate isopropylamine salt	Herbicide
Mesosulfuron	Jiajierhuanglong	30 g L^{-1} Mesosulfuron-methyl	Herbicide
Oxyfluorfen	Guo'er	240 g L^{-1} Oxyfluorfen	Herbicide
Paraquat	Baicaoku	200 g L^{-1} Paraquat	Herbicide
Pendimethalin	Xiaocao'an	330 g L^{-1} Pendimethalin	Herbicide
Tribenuron-methyl	Benhuanglong	40% Tribenuron methyl	Herbicide
Chlorpyrifos	Dusibi	40% Chlorpyrifos	Insecticide
Chlorpyrifos-phoxim	Duxin	10% Chlorpyrifos 30% Phoxim	Insecticide
Decis	Dishasi	25 g L^{-1} Decamethrin	Insecticide
Dichlorvos	DDV	77.5% Dichlorvos	Insecticide
Dimethoate	Leguo	40% Dimethoate	Insecticide
Dipterex	Dibaichong	90% Trichlorphon	Insecticide
Imidacloprid	Pichonglin	50% Imidacloprid	Insecticide
Lambda-cyhalothrin	Kungfu	5% Lambda-cyhalothrin	Insecticide
Matrine	Kusenjian	0.36% Matrine	Insecticide
Omethoate	Yanghualeguo	40% Omethoate	Insecticide
Oxadixyl.mancozeb	Shadufan	6% Oxadixyl 58% Mancozeb	Insecticide
Parathion[c]	Duiliulin	Parathion	Insecticide
Phoxim[c]	Xinliulin	25%/40% Phoxim	Insecticide
Phoxim-phorate	Jiabanlin	10% Phoxim-phorate	insecticide
Pyridaben	Damanlin	15% Pyridaben	Insecticide

a: the name was registered in China; b: the commercial name is used in China; c: the pesticide was banned.

The commonly applied pesticides in the study area are listed in Table 2.6, based on the information and permission of the retailers. Insecticides were used more frequently than fungicides and herbicides at a ratio of 2:1:1. Some organophosphorous pesticides had already been banned, but some such as parathion and phoxim were still available in the stores.

2.3.5 Farmer and retailer awareness of the dangers of pesticides to human health and the environment

The investigation of the awareness of the dangers of pesticide use to human health and the environment provided interesting results in these two selected regions (Table 2.7). Over half of the interviewees declared they knew that pesticides left residues. In S2, 92.1% of the interviewed people believed that pesticides were harmful to human health, but 46.9% of the people in S1 held the opposite attitude on this affair (p<0.01). Opinions on the effects of pesticides on the environment were significantly different: 43.6% of the people in S2 thought that pesticides could affect environmental quality, but 49.2% of the interviewees in S1 "had no idea" (p<0.01). More specifically, the similar proportions in these two regions suggested that water pollution was seen to be related to pesticide use, but most farmers did not clearly understand the relationship between them. Furthermore, S1 and S2 differed significantly in the understanding of the relationship between illness and pesticides (p<0.01). The majority of farmers (79.7%) in S1 did not think that illness was related to pesticide use. In contrast, 67.3% of the interviewees in S2 were certain of the relationship, and very few denied it. The proportion of people in S2 who knew nothing about the relationship between illness and pesticides was similar to the proportion of people in S1 who admitted that illness was related to pesticides.

Table 2.7 *Awareness of pesticides risk on environment and health of interviewees (farmers and retailers)*

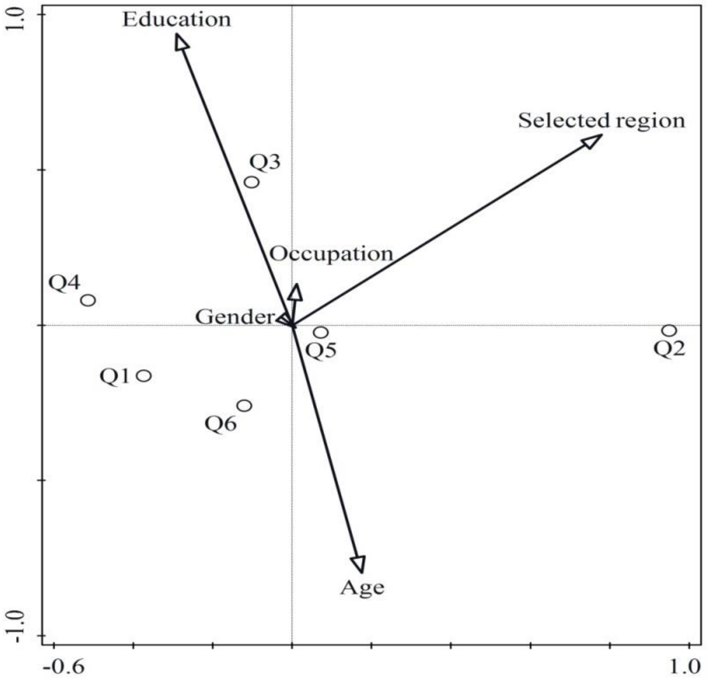
Questions	Variables	Qianyang (N=128)		Chencang (N=101)	
		No.	%	No.	%
Do you know pesticide residues?					
χ^2=0.5	Yes	69	53.9	54	53.5
	No	29	22.7	27	26.7
	Have no idea	30	23.4	20	19.8
Do you think pesticides are harmful for human health?					
χ^2=85.9**	Yes	36	28.1	93	92.1
	No	32	25.0	1	1.0
	Have no idea	60	46.9	7	6.9
Do you think environment can be impacted by pesticides?					
χ^2=18.0**	Yes	23	18.0	44	43.6
	No	42	32.8	31	30.7
	Have no idea	63	49.2	26	25.7
Do you think water pollution is related with pesticide application?					
χ^2=0.9	Yes	40	31.3	37	36.6
	No	30	23.4	19	18.8
	Have no idea	58	45.3	45	44.6
Do you think illness is related with pesticide application?					
χ^2=58.9**	Yes	26	20.3	68	67.3
	No	59	46.1	5	5.0
	Have no idea	43	33.6	28	27.7
Do you know how to handle the risk of pesticides?					
χ^2=1.0	Yes	72	56.3	64	63.4
	No	0	0	0	0
	Have no idea	56	43.7	37	36.6
Measurements to reduce the risk of pesticide application					
χ^2=18.8**	Reduce dose	16	12.5	11	10.9
	Use protection	36	28.1	12	11.9
	Recycle container	40	31.3	62	61.4
	Low toxic instead	25	19.5	40	39.6

Significant difference between the study regions: ** $p<0.01$

Most of the people in these two regions knew how to deal with the dangers of pesticides, but nearly 40% did not. The methods used to avoid the dangers of pesticides differed between the two areas ($p<0.01$). In S1, 31.2 and 28.1% of the people assumed that recycling the containers and using protective measures, respectively, would reduce the risks, followed by using less toxic pesticides (19.5%) and reducing the pesticide dosage (12.5%). In S2, 61.4% of the people thought that recycling the containers was the best way to reduce risks, and 39.6% thought that using less toxic pesticides was also an important method. Using protective measures (10.9%) and reducing the dosage of pesticides (11.9%) were only considered as alternative methods.

The dominance tendency of the perception shows overall resemblance among interviewees and doesn't reveal any major influencing factors. For this reason, a statistical method, canonical correspondence analysis (CCA), was used to implement a factorial analysis. CCA analysis was performed on the basis of backgrounds of interviewee (Table 2.2) and revealed perception of pesticide risks (Table 2.7). The perception-background relationship is depicted in Figure 2.2, an ordination diagram in which the first two canonical axes are in the horizontal and vertical direction, respectively, and the arrows represent the different background variables.

The direction of the arrows represents the correlation between each variable and the canonical axes ,and each other, whereas the length of the arrows represents the relative a contribution of the variables to the axes and the perception-background relationship. Generally, the first canonical axes represents an estimated 71.6% of the variation in the perception-background of pesticide risk and the first two represent an estimated 86.9%. Selected region, education, and age were significantly correlated with the responses to the dangers of pesticides (permutation test, $p<0.01$) (Table 2.7), but occupation and gender were not (Figure 2.2). The opposite directions of the arrows for education and age in Figure 2.2 indicated that these two factors had opposite influences on the awareness of the dangers of pesticides. The location of gender and occupation near the origin of the coordinates indicated that the effects of these two factors on the understanding of the dangers of pesticides were similar and could not vary the percentage of the explanation of understanding on the canonical axis. Consequently, selected region, education, and age were important factors in promoting the understanding of the dangers of pesticides to the environment and human health.



Q1: Do you know pesticide residues? Q2: Do you think pesticides are harmful for human health? Q3: Do you know environment can be impacted by pesticides? Q4: Do you think water pollution is related with pesticide application? Q5: Do you know the relationship between pesticides and illness? Q6: Do you know how to handle the risk of pesticides?

Figure 2.2 *Biplot of perception of pesticide risks and backgrounds of interviewees under CCA as constructed according to data collected. Full questions are presented in Table 2.1c*

2.4 Discussion

The level of knowledge of pesticides of the stakeholders is vital for providing sound strategies for reducing environmental and health risks. As the end sellers and users, retailers and farmers play important roles in the safety of pesticide use, especially in rural areas. This study was intended to evaluate the attitudes and levels of awareness of pesticide safety to address reasonable measures for avoiding the dangers of pesticides and for reducing potential pollution to agricultural systems. Men appeared to take more responsibility than did women to purchase and spray pesticides which is related the roles acted in the family. The gender-specific knowledge of pesticide use seems to be a precaution to the dangers of exposure (Atreya, 2007), especially for women living in rural regions (Cui, 2009). Age and educational level differed significantly in our study between the two regions. The levels of knowledge of pesticide safety were insufficient in older and less educated interviewees. Recena et al. (2006) and Ibitayo (2006) reported that a low level of education among farmers hampered their ability to follow the hazard warnings provided by the chemical industry and regulatory agencies. The lack of education has been associated with poisonings, suicides, exposure risks, and high mortality rates in many rural areas of developing countries (Phillips et al., 2002; Zhou et al., 2011; Zyoud et al., 2010).

Salameh et al. (2004) claimed that adequate and reliable sources of information seemed to induce the perception of risk and the adoption of preventive measures, despite the low general level of education of the subjects involved. Oral communication with retailers and among farmers played a dominant role in learning about pesticides and their functions. Although some media channels provide information about the control of pests and diseases in cultivation, media advertising seems an inadequate mean to provide information about pesticides. Participants said that information provided by television was difficult to apply because of differences from the real conditions of cultivation. The distrust of pesticide advertisements led to a strong reliance on the information provided by distributors and neighbours and on the personal experience of the farmers. Accordingly, based on their own experiences, farmers would likely overuse or mix pesticides unaware of the negative interactions among the various active ingredients. Mixed pesticides not only lose efficacy but may also enhance the hazards to the sprayer and the environment (Karunamoorthi et al., 2011).

Correct application, proper protective measures, and good personal hygiene are considered to be good practices for the safe spraying of pesticides (Matthews, 2008). Dasgupta et al. (2007) reported that increasing the use of protective measures could decrease the probability of poisoning by 44.3%. The lack of protective measures can lead to unpredictable hazards when farmers load their sprayers and walk through their treated crops (Recena et al., 2006). The high incidence of adverse symptoms (intoxication) such as cephalea, dizziness, vomiting, and skin problems have been reported after pesticide use (Ngowi et al., 2007a; Ngowi et al., 2007b; Recena et al., 2006; Yassin et al., 2002). Most respondents in our study said that they applied pesticides without taking any protective measures. They also claimed that special protective gear, such as waterproof clothes or masks, were uncomfortable to wear in summer and even, in some cases, unnecessary during the limited time of spraying. In addition, personal hygiene, e.g. washing hands, changing clothes, and showering, is another way to avoid poisoning after pesticide application (Dasgupta et al., 2007). Unfortunately, some farmers ignore such measures, which is circumstantial evidence that the danger of poisoning is higher when no precautions are taken when using pesticides (Ngowi et al., 2007a).

The methods of storing and disposing of pesticide containers are also critical points of intervention to enhance the awareness of safety during the application of pesticides (Matthews, 2008). Storing pesticides in the home can easily contaminate drinking water and food and can threaten the health of children. Matthews (2008) reported that 62% of 8500 smallholders in 26 countries stored pesticides, and 68% of this group stored the pesticides in locked locations. Similarly, over 50% of the farmers in our survey stored pesticides, but approximately half of this group stored them in their homes. The interesting point is that about 40% of the farmers had never stored pesticides, which is a good option for reducing the dangers of pesticides. Some larger countries recycle pesticide containers despite having contained dangerous chemicals (Matthews, 2008; Salameh, 2004). We often observed farmers discarding empty plastic bags and bottles in wells or ditches where the pesticide solutions were prepared. This observation was supported by the responses of the interviewed farmers. Pesticide residues in empty containers may be released or washed into the surroundings by rain and/or irrigation. This uncontrolled discharge of pesticide pollutants can easily contaminate agricultural soil and water and also threaten human health and ecosystem quality (Hvistendahl, 2013; Ibitayo, 2006). The responses and practices of the farmers suggested that S1, a hilly area with severe soil erosion, was at a greater risk than S2 to the dangers of pesticide use.

Since the publication of Rachel Carson's *Silent Spring*, more attention has been paid to the problems triggered by pesticides. Several pesticides have been banned in the last three decades due to their ecotoxicities and long half-lives. The reasons for these bans were not clear to the farmers. Some environmentally friendly pesticides are produced, but a few banned pesticides are still commercially available (Table 2.6). Effective legislation and strict supervision should be improved to monitor the production and circulation of pesticides. Admittedly, economics is another factor why farmers ignore the dangers of pesticides (Uri, 1998). Farmers claimed that expenditure was an important factor in the purchase of pesticides. Our survey and calculations, however, indicated that expenditures on pesticides were less than 3% of the total agricultural income, so farmers were not likely to reduce pesticide use for economic reasons. Furthermore, pesticide consumption and use involves several stakeholders, such as authorities, producers, retailers, and farmers. The owners of local pesticide stores, as the final links in the economic chain, play an important role in disseminating pesticides and guiding their use for farmers and agricultural workers. In this study, most retailers provided guidance to farmers on the use of pesticides and on the protective measures available for their application. The retailers, however, revealed that farmers were reluctant to adopt these measures, preferring to rely on their own experience and the influence of their neighbours and ancestors (Matthews, 2008; Yassin et al., 2002; Zyoud et al., 2010). Compared to farmers, retailers were either more familiar with the products or were more aware of the reasons why some pesticides had been banned, implying that the retailers in the study areas have the ability to interpret and provide advice on the active ingredients, functions, and application dosages of pesticides.

The perception of risk is an important element in developing effective campaigns of education and communication (Damalas et al., 2008). The prevalence of pesticide poisoning decreased from 1.05 to 0.25% after a safety educational programme (Chen et al., 1998). An awareness of the dangers of pesticides to the environment and human health reflects a consciousness of self-protection and a responsibility to the surroundings (Ibitayo, 2006). In our study, only some of the basic information on pesticide residues was known, and the levels of awareness of the dangers of pesticides to human health were significantly different between the selected areas. Some aspects of the relationships between pesticides and environmental factors and human health were unclear and sometimes unknown. Gender, age, educational experience, and even location were all correlated with vague responses (Figure 2.2). These correlations suggest that educational programmes should be specifically targeted to improve the self-protective consciousness of farmers to the use of pesticides, especially in the rural regions of developing countries.

2.5 Conclusions

This study indicated that farmers are exposed to the dangers of pesticides in the Wei River catchment, especially in S1, a hilly region. Even though some protective measures are taken, the farmers seem to be unaware of the true risks from the use of pesticides. Retailers are well-informed and have a strong understanding of, and sense of responsibility towards, pesticide application. The awareness of the dangers of pesticides to human health and the environment, however, is still limited in these two study areas. The canonical coordination analysis indicated that older and poorly educated people are most at risk.

Therefore, measures to reduce pesticides risks can be grouped into three categories:

1.) Those related to applying pesticides (farmers and retailers).
2.) Those related to producing pesticides (factories).
3.) Those related to supervising pesticides (authorities).

According to this survey, the steps for reducing pesticide effects on farmers would be considered. The pressing step, supposedly, is to implement some educational programmes for farmers in non-harvesting time (normally in winter). Understandable activities, such as lectures, pictures, videos and some interesting shows which reflect the pesticide risk on health and environment, can be held based on farmers' age in rural regions. At the same time, many strict procedures on pesticide registration should be concerned and the detail information of pesticides should be labelled especially marking the level of toxicity for human health. The supervisory mechanism and environmental monitoring systems for pesticides should be strengthened and the nation scale survey on safety use of pesticide and its risk on environment and human health should also be evaluated. The large agricultural population in China suggests that all stakeholders, including governmental agencies, producers, retailers, and farmers, should unite to address the risks from the use of pesticides for farmers and the environment.

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3 Short-term transport of glyphosate with erosion in Chinese loess soil – a flume experiment

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^{-2}), and a rain intensity of 1.0 mm min^{-1} 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 relative 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 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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3.1 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 d (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; Zablotowicz et al., 2009).

Glyphosate strongly adsorbs on soil particles by ligand exchange through the phosphonic acid moiety (Sheals et al., 2002a; 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 on-site (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., 2005a; 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., 2004b; 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 77d 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 was 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., 2011a; Vinten et al., 1983). Based on 28 months of field monitoring, 99% of the lost glyphosate (5.12 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., 2011b). 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 propose 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 off-site pollution was discussed due to the threats to neighbouring areas of glyphosate application followed directly by rain.

3.2 Materials and methods

3.2.1 Experimental design

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 $\mu g\ g^{-1}$) and AMPA (0.01 $\mu g\ g^{-1}$) was detected before we operated the experiment. The soil properties are shown in Table 3.1.

Table 3.1 *Principle properties of selected soil (n=6)*

Properties	Value
Particle size distribution:	
<0.002 mm (clay) (%)	28.5±0.4
0.002-0.02 mm (%)	43.5±1.3
>0.02 mm (%)	28.0±0.8
Bulk density (g cm^{-3})	1.4±0.1
pH (H_2O)	8.1±0.1
EC (µS cm^{-1})	146±1.2
Cation exchange capacity (CEC) (cmol kg^{-1})	18.3±0.6
Organic matter (g kg^{-1})	7.6±0.3
Total phosphorous (g kg^{-1})	0.7±0.01
Available phosphorous-Olsen (mg kg^{-1})	17.0±0.1
Total Al (g kg^{-1})	27.5±0.2
Total Fe (g kg^{-1})	32.6±1.0
$CaCO_3$ (g kg^{-1})	53.7±0.6
Total Nitrogen (g kg^{-1})	1.5±0.1

Design

We designed the experiments to test the short-term transport of glyphosate (360 mg m^{-2} and 720 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 mm min^{-1}, representing a typical rain storm in this region of China (Cai et al., 1998). The treatments (T1: 360 mg m^{-2}, 10°; T2: 360 mg m^{-2}, 20°; T3: 720 mg m^{-2}, 10°; T4: 720 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 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 g cm^{-3}, and the lower four layers had bulk densities of 1.35 g cm^{-3}, which simulated field conditions monitored when soils were taken. The full-filled flumes were pre-wetted under a 0.5 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 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.

3.2.2 Glyphosate application and sampling

The commercial product *Roundup®* (Monsanto, produced in Malaysia, Sinochem Agent), glyphosate-based herbicide, containing 360 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 g L^{-1} and 0.72 g L^{-1}) at a nozzle distance of 5 cm above the soil surface of each flume (0.4 m^{-2}) before being exposed to 1 mm min^{-1} rain. Then the rate of glyphosate applied was 360 and 720 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 hours after applied. Based on this, extremely case was simulated that rain occurs 30 min after glyphosate 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 °C until analysis.

3.2.3 Glyphosate and AMPA determination

3.2.3.1 Chemicals and solvents

Glyphosate (98%) and AMPA (98.5%) reference standards were obtained from Sigma-Aldrich (USA). Isotopically-labelled glyphosate (1, 2-^{13}C, ^{15}N; 100 µg·mL^{-1}, 1.1 mL) and AMPA (^{13}C, ^{15}N; 100 µg·mL^{-1}, 1.1 mL), used as internal standards, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). FMOC-Cl (9-fluorenylmethoxycarbonyl chloride, ≥99.0%) was purchased from Sigma-Aldrich (Switzerland). Sodium tetraborate decahydrate, a tetraborate buffer (≥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 (≥98% p.a.) was purchased from Merck (The Netherlands). Ammonium acetate (NH_4Ac, approximately 98%) from Sigma (USA) and ammonia solution (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 µg mL^{-1} mixed with the isotope-labelled standards (5 µg 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 °C.

3.2.3.2 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 µL of 6 M HCl were 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 µg 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 µL of concentrated formic acid. All samples were then shaken manually, and 0.5 mL was transferred to plastic LC vials integrated with 0.45 µm PFTE filters. All samples were prepared in duplicate. The solvent standards were derivatised with the samples for each batch of samples.

3.2.3.3 LC-MS/MS

Glyphosate and AMPA concentrations were determined by LC-MS/MS using an XBridge™ Shield RP C18 column (3.5-µm particle size, 150 mm in length, 2.1-mm i.d.) (Waters, The Netherlands). The mobile phases consisted of 5 mM NH_4Ac in Millipore water (solvent A, pH=9) and a 9:1 MeOH:H_2O (Millipore) solution (solvent B, pH=9). The pH was adjusted to approximately 9 using 25% 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 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 h^{-1} (cone) and 580-600 L h^{-1} (desolvation). The transitions acquired for the FMOC derivatives of glyphosate, AMPA, and their corresponding labels are given in Table 3.2.

Table 3.2 *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
$^{13}C^{15}N$ 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-$^{13}C_2$ ^{15}N Glyphosate-FMOC	390.20	Q: 171.10	0.05	12.00

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

3.2.3.4 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 µg mL^{-1} indicated satisfactory linearity, with correlation coefficients >0.99 and residuals lower than ±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 µg g^{-1}. Spiked water samples were analysed in quintuplicate at concentrations of 0.01 and 0.5 µg 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 3.3. The limits of quantification (LOQ), defined as the lowest concentration tested for which an average recovery between 70-120% and a relative standard deviation ≤20% are obtained, were 0.05 µg g^{-1} for soil and 0.01 µg mL^{-1} for water, for both glyphosate and AMPA. The limits of detection (LOD) (S:N=3) were 0.030 µg g^{-1} for glyphosate and 0.039 µg g^{-1} for AMPA in soil and 0.0067 and 0.0074 µg 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 µg mL^{-1}.

Table 3.3 *Summary of validation data*

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

3.2.4 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:

$$R = \frac{V}{A \times t} \qquad [3.1]$$

$$E = \frac{m_{sus}}{A \times t} \qquad [3.2]$$

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

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

$$m_{Tg} = \frac{\sum_i^n (V \times C_{rg}) + \sum_i^n (m_{sus} \times C_{susg})}{1000 \times A} \qquad [3.3]$$

$$m_{Ta} = \frac{\sum_i^n (V \times C_{ra}) + \sum_i^n (m_{sus} \times C_{susa})}{1000 \times A} \qquad [3.4]$$

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

$$m_{sg} = \frac{\sum_j^k (m_{sj} \times C_{sgj})}{1000 \times A} \qquad [3.5]$$

$$m_{sa} = \frac{\sum_j^k (m_{sj} \times C_{saj})}{1000 \times A} \qquad [3.6]$$

where m_{sg} is the total amount of glyphosate in the soil, mg m^{-2}; m_{sa} is the total amount of AMPA in the soil, mg m^{-2}; m_{sj} is the soil weight in the jth soil layer, g; C_{sgj} is the glyphosate content of the jth soil layer, µg g^{-1}; C_{saj} is the AMPA content of the jth soil layer, µg 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:

$$R_d = \frac{m_{Tg}+m_{sg}+1.52\times(m_{Ta}+m_{sa})}{m} \times 100\% \quad [3.7]$$

Where R_d is the recovery of glyphosate, %; m is the applied glyphosate in each flume, 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.

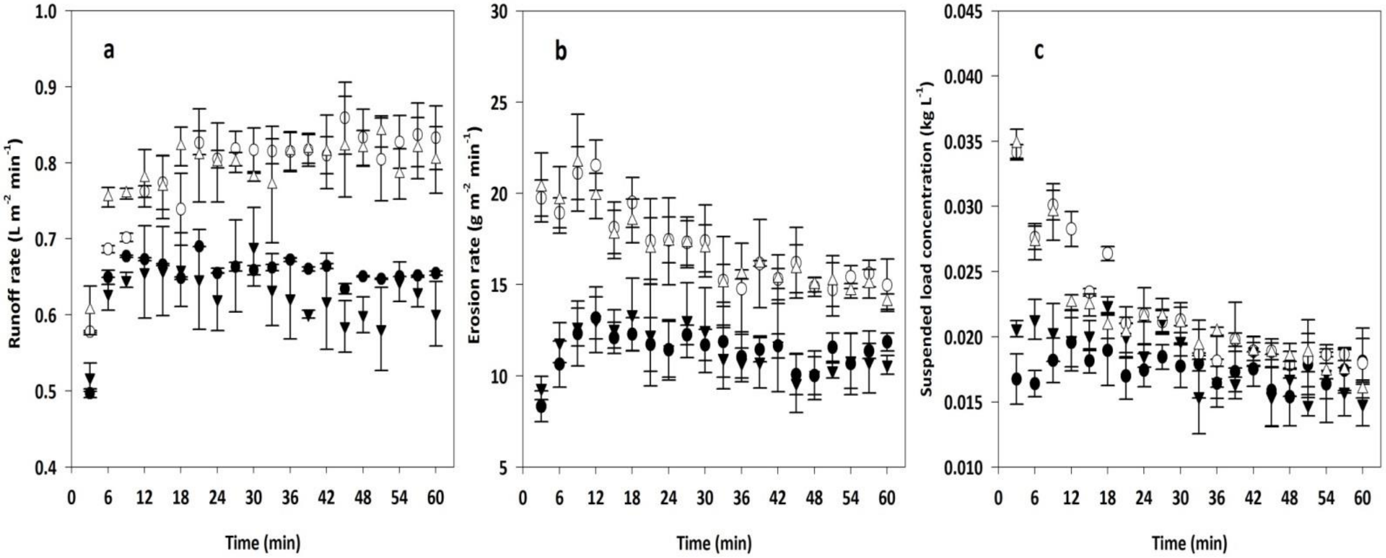


Figure 3.1 *Temporal variation in the runoff rate, erosion rate and suspended load concentration in different treatments: (a) runoff rate, (b) erosion rate, (c) suspended load concentration*

3.3 Results

3.3.1 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 (Figure 3.1). In the 10° slope treatments (T1, T3), runoff rate increased in the first 15 min and then reached a steady-state at 0.64±0.01 L m^{-2} min^{-1}. In the 20° slope treatments (T2, T4), runoff rate increased in the first 21 min then steadied at 0.82±0.01 L m^{-2} min^{-1} (Figure 3.1a). Erosion rate increased in the first 15 min in T1 and T3 but then decreased to a rate of 13.18±0.71 g m^{-2} min^{-1} in T1 and 11.06±1.97 g m^{-2} min^{-1} in T3. The erosion rate in T2 and T4, however, peaked in the first 9 min at 23.11 g m^{-2} min^{-1} and then declined gradually to steady states of 18.86±2.49 and 17.16±1.17 g m^{-2} min^{-1} in T2 and T4, respectively (Figure 3.1b). Suspended load concentration differed significantly in the first 9 min of 10° and 20° slope treatments ($p<0.05$) and then levelled 0.0175±0.01 and 0.0196±0.02 Kg L^{-1}, in 10° (T1 and T3) and 20° (T2 and T4) (Figure 3.1c). Therefore, runoff and erosion rate were significantly different between the two slope gradients ($p<0.05$) while suspended load concentration was relative constant (Figure 3.1a-c).

3.3.2 The distribution of glyphosate and AMPA in the runoff and suspended load

3.3.2.1 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 (Figure 3.2a). The maximum of glyphosate concentration was detected in the first 3 min, 1.64 and 1.12 µg mL^{-1} in T1 and T2 and 2.90 and 2.75 µg 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±0.02 µg mL^{-1} in T1/T2 and 0.17±0.03 µg mL^{-1} in T3/T4 after 42 min of rain. Similarly, the AMPA concentrations in the runoff peaked at 0.03 and 0.02 µg mL^{-1} in T1 and T2 and 0.08 and 0.04 µg 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 µg mL^{-1} in T3/T4 and T1/T2, respectively, after 42 min (Figure 3.2b). It is clear that the AMPA concentration in T3 and T4, treated with a higher amount of glyphosate, however, were 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) (Figure 3.2a-b).

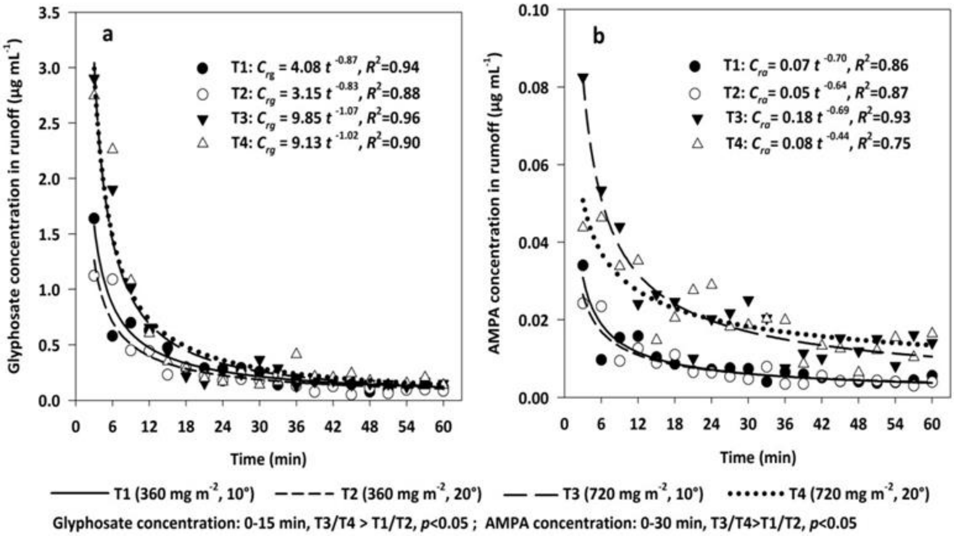
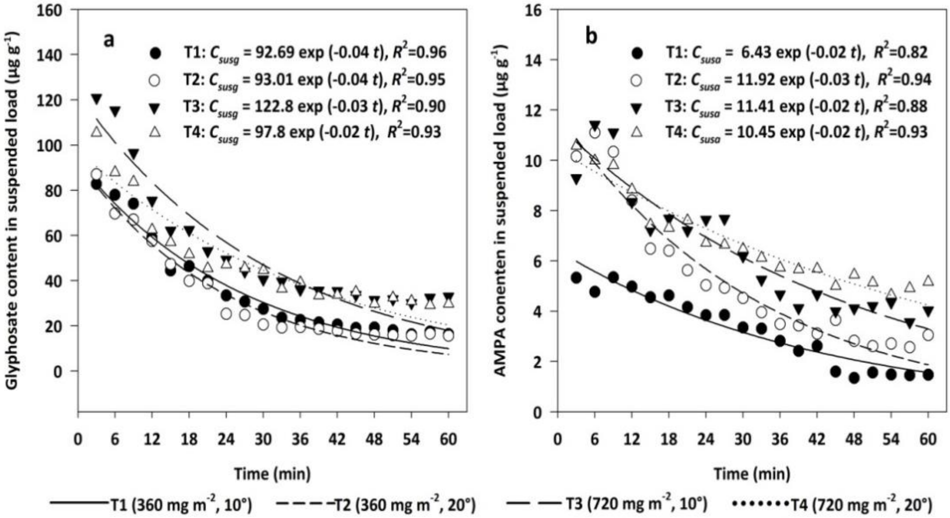


Figure 3.2 *Glyphosate and AMPA concentration in runoff of different treatments: (a) glyphosate concentration in runoff (T3/T4>T1/T2, p<0.05, 0-15 min), (b) AMPA concentration in runoff (T3/T4 >T1/T2, p<0.05, 0-30 min)*

3.3.2.2 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 (Figure 3.3a-b). The glyphosate content was slightly higher (but not significantly) for the lower slope gradient (10°) than for the higher gradient (20°) 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±2.99 to 24.05±4.97 µg g^{-1} in T1 and T2 and from 113.11±11.05 to 42.57±2.88 µg g^{-1} in T3 and T4, respectively. Thereafter, the glyphosate content decreased more gradually, reaching relatively steady levels of 17.98±2.36 in T1/T2 being significant lower than 32.92±2.98 in T3/T4 (Figure 3.3a). The AMPA content, however, was higher for the 20º 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 was observed at the first 15 min and then decreased without significant differences in treatments (*p*<0.05) (Figure

3.3b). According to the content of glyphosate and AMPA in the suspended load, a strong significant exponent relationship was estimated with rain duration (Figure 3.3a-b).



Glyphosate content: 0-15 and 30-60 min, T3/T4>T1/T2, p<0.05; AMPA content: 0-15 min, T3/T4>T1/T2, p<0.05.

Figure 3.3 *Glyphosate and AMPA content in suspended load in different treatments: (a) glyphosate content in suspended load, (b) AMPA content in suspended load*

3.3.3 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 3.4). The glyphosate content in the surface soil differed significantly in treatments, with 8.12/8.28 and 21.29/18.91 μg 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.

Table 3.4 *Glyphosate and AMPA content in different soil depth of treatment (n=3)*

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

The content of glyphosate and AMPA is given as means ± standard deviations.
The means followed by the same letter do not differ at the 95% confidence level.
*Glyphosate and AMPA was detected but the content was below LOQ.

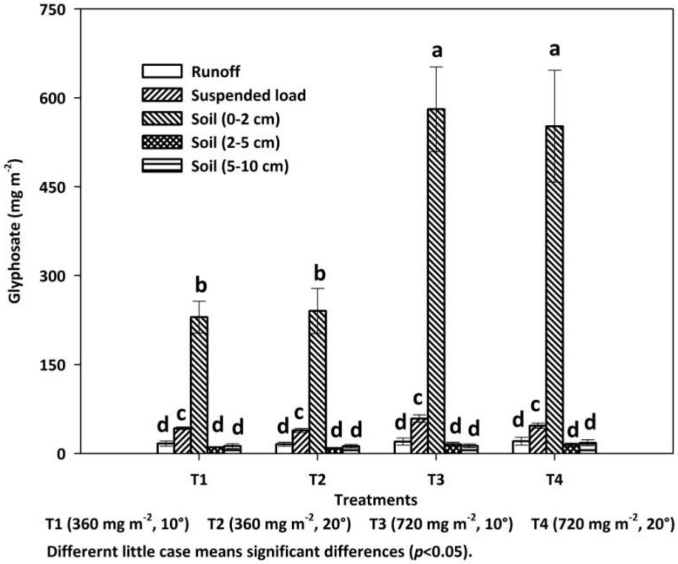


Figure 3.4 *Glyphosate fate in short-term simulation rainfall of treatments*

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 3.5). 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 double the rate 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±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 was very limited, only 2 and 3% in the 2-5 and 5-10 cm layers, respectively. In total, 76±6% of the applied glyphosate was detected in runoff, suspended load and soil after an hour rainfall and the recovery of glyphosate was as high as 91±4% calculating AMPA as parent glyphosate (mass balance).

3.4 Discussion

With the increase 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., 2004a; 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 off-site 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., 2011a). 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 µg L^{-1} of glyphosate was detected which is ten times of the EU limit value (0.1 µg L^{-1}) for this herbicide in groundwater while the level of glyphosate/AMPA in public water

Table 3.5 *Glyphosate transport with runoff and sediment in the first hour after application*

Treatment	Applied glyphosate (mg m^{-2})	Glyphosate transported by runoff* (mg m^{-2})				Glyphosate transported by suspended load* (mg m^{-2})				Sum (mg m^{-2})	Transport rate (% h^{-1})
		∑ 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%

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

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 increase 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 g mL^{-1}, 20 °C) and desorption in soil matrix (Gimsing et al., 2004b). Once soil erosion occurs, the bound glyphosate and AMPA can be detached and washed together with soil particles (Degenhardt et al., 2012; Todorovic et al., 2014). Regarding to 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 Degenhardt 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 is rare (Schulz, 2004). Therefore, the gap in this field needs to be concerned due to glyphosate properties and its intensive use (Zhang et al., 2011b).

The chemicals transported via soil macropores during intensive rain may enhance the movement of substances (Jarvis, 2007; Lowry et al., 2004; Styczen et al., 2011a). 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, extremely 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; Zablotowicz 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 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 is 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 on-site 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 ninety percent 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 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.

3.5 Conclusions

Glyphosate being applied before and after sowing to bare loess soil leads to strongly risk for off-site transport if rainfall occurs shortly after application. Particulate-facilitated transport is the mainly mode for glyphosate contaminating off-site. The risk of glyphosate retained in top soil is high and the efforts on reducing contamination in off-site needs 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 off-site, several practical work or guideline 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; 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.

Acknowledgements

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

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 days after the application. Glyphosate and AMPA concentration in runoff were low while the contents in the sediment was much higher than in the upper 2 cm of the soil.

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Yang X., Wang F., Bento C.P.M., Lei M., Van Dam R., Mol H., Liu G., Ritsema C.J., Geissen V.
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4.1 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 on-site or be transported off-site 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; Bergström 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., 2004b; 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., 2002b). 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., 2002b; 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; Bergström et al., 2011; Gimsing and Borggaard, 2002; Gimsing et al., 2004a; Gjettermann et al., 2011; Rampazzo et al., 2013; Sprankle et al., 1975; Strange-Hansen et al., 2004; Wang et al., 2006; Wang et al., 2005b; 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; Bergström et al., 2011; Giesy et al., 2000b; 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; Bergström et al., 2011; Kjaer et al., 2005; Lanctot et al., 2013; Londo et al., 2014; Styczen et al., 2011b; 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 (Bergström 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., 2014a; Zhang et al., 2011b), which underlies a high risk of transport by processes associated with erosion (Al-Rajab and Schiavon, 2010; Laitinen et al., 2009; Styczen et al., 2011b; 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 on-site accumulation and off-site pollution.

4.2 Materials and methods

4.2.1 Study area

This study was conducted 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 4.1).

4.2.2 Experimental design

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., 2014a). 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.

Table 4.1 *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 (%)	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 (µS 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

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 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.

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-mLplastic 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 moisture and one for glyphosate determination. All samples were stored at -24 °C until analysis.

4.2.3 Glyphosate and AMPA analysis

Chemicals

Glyphosate (98%), AMPA (98.5%), sodium tetraborate decahydrate (≥99.5%), and ammonium acetate (approx. 98%) were purchased from Sigma-Aldrich Co. (USA). Isotopically labelled glyphosate (1,2-^{13}C, ^{15}N; 100 µg mL^{-1}; 1.1 mL) and AMPA (^{13}C, ^{15}N; 100 µg mL^{-1}; 1.1 mL), used as internal standards, were obtained from Dr. Ehrenstorfer (Augsburg, Germany). FMOC-Cl (9-fluorenylmethoxycarbonyl chloride) (≥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 Actu-All Chemicals (The Netherlands). Formic acid (p.a., ≥98%) was obtained from Merck (The Netherlands).

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., 2015b). 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 µm particle size, 150 mm × 2.1 mm i.d. column (Waters, The Netherlands). All the parameters of methods were described by Yang et al (2015).

4.2.4 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, µg g^{-1}) in the upper 2 cm of soil were 15 µg g^{-1} for treatments S1G1 and S2G1 and 30 µg g^{-1} for S1G2 and S2G2, calculated by:

$$C_0 = \frac{m \times 1000}{A \times d \times \rho_b} \qquad [4.1]$$

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:

$$\frac{C_t}{C_0} = e^{-kt} \qquad [4.2]$$

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

$$DT_{50} = \frac{\ln 2}{k} \qquad [4.3]$$

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

$$T_{loss} = \frac{\sum(C_{rg} \times V + 1.52 \times C_{ra} \times V) + \sum(C_{sg} \times m_s + 1.52 \times C_{sa} \times m_s)}{10^6} \qquad [4.4]$$

where C_{rg} is the glyphosate concentration of the runoff, µg mL^{-1}; C_{sg} is the glyphosate content of the sediment, µg g^{-1}; C_{ra} is the AMPA concentration of the runoff, µg mL^{-1}; C_{sa} is the AMPA content of the sediment, µg g^{-1}; $\mathrm{m_s}$ 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}) were 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:

$$R_{loss}\ (\%) = \frac{T_{loss}}{T} \times 100\% \tag{4.5}$$

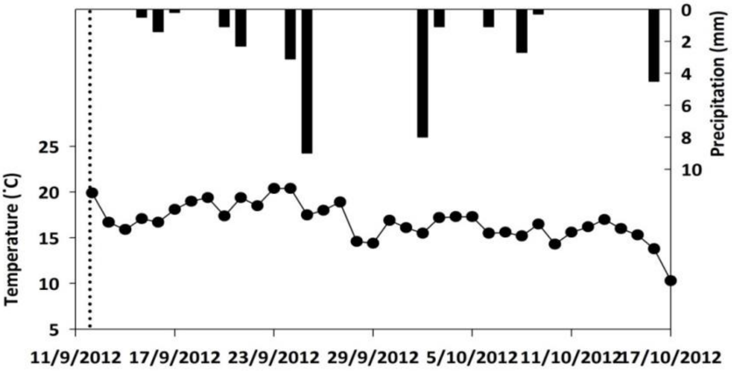
where T is the initial amount of glyphosate applied, 3.6 kg a.i. ha^{-1} or 7.2 kg a.i. ha^{-1} in this study.

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.

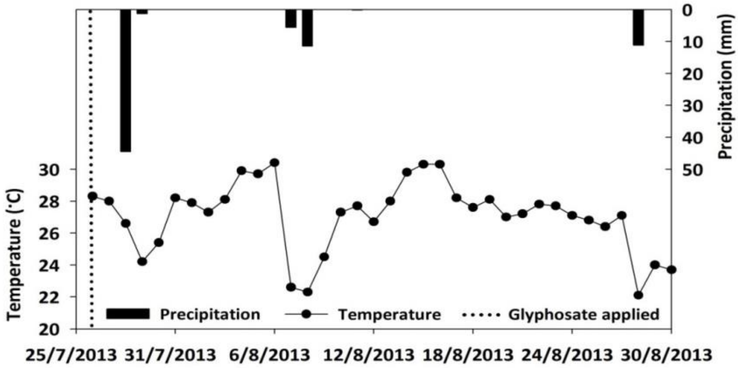
4.3 Results

4.3.1 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 (Figure 4.1). In 2012, no erosive rains fell during the monitoring period, which had an average temperature of 16.8±2.1 °C (Figure 4.1a). 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 (Figure 4.1b). Soil moisture in the surface layer (0-2 cm) correspondingly changed when it rained but did not vary at different slopes (Figure 4.2). The initial soil moisture was higher in 2012 than in 2013, and dynamic changes were observed due to the rain (Figure 4.2a,b).



(a) Observation periods in 2012



(b) Observation periods in 2013

Figure 4.1 *Precipitation and temperature of monitoring periods in 2012 (a) and 2013 (b)*

4.3.2 Glyphosate decay

Glyphosate and AMPA residues

Glyphosate and AMPA were detected in all soil samples from all layers in 2012 (Table 4.2 and 4.3). 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 4.2), while the AMPA content increased in the first 3 d and then decreased (Table 4.3). 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.

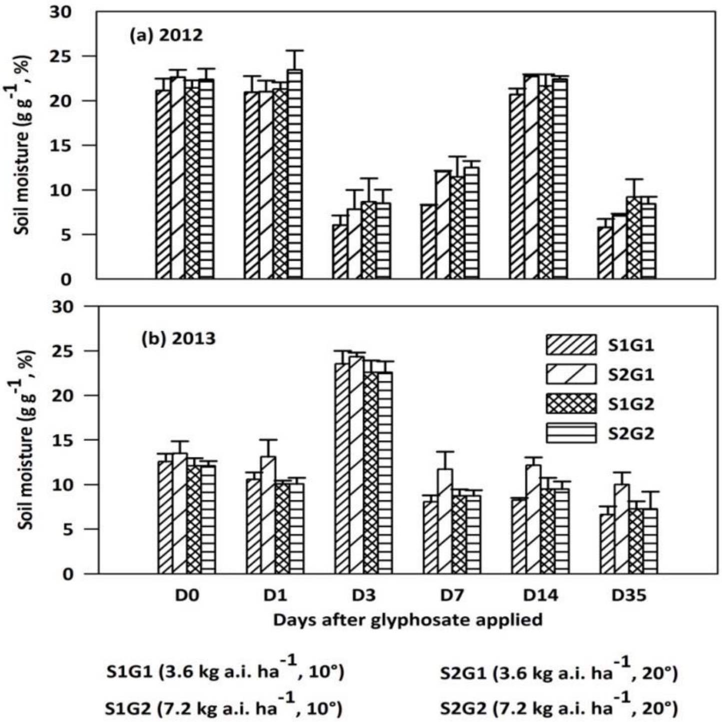


Figure 4.2 *Soil moisture in upper 2 cm soil days after glyphosate application in 2012 (a) and 2013 (b)*

Table 4.2 *Glyphosate residues in different soil layers of the different treatments (2012)*

Treatment	Soil depth (cm)	Glyphosate residues before and after days from application (µg 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±0.01b	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 means significant difference between the soil layers at the same time ($p<0.05$);

* means the results lower than the detection limit;

means the residues of glyphosate in soil layers on the day before glyphosate applied;

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°).

Table 4.3 *AMPA residues in different soil layers of the different treatments (2012)*

Treatment	Soil depth	AMPA residues before and after days from application (μg g^{-1})					
	(cm)	$0^{\#}$	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 means significant difference between the soil layers at the same time (p<0.05);

* means the results lower than the detection limit;

means the residues of AMPA in soil layers on the day before glyphosate applied;

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°).

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 (Figure 4.3). 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 (Figure 4.3a) and 2013 (Figure 4.3b) at the same treatment.

Interestingly, the intercepts of the regression equations in different treatment were close to the initial amount of added glyphosate. Supposedly, there was no drift and loss on the day when glyphosate was sprayed. Then the best fit regression curve of the glyphosate decay data are shown in Figure 4.4 (p<0.01, n=72):

$$\frac{C_t}{C_0} = 0.97\, e^{-0.18\, t} \quad (p<0.01,\ R^2=0.95,\ \mathrm{n}=72) \qquad [4.6]$$

$$\frac{C_t}{C_0} = 0.93\, e^{-0.17t} \quad (p<0.01,\ R^2=0.91,\ \mathrm{n}=72) \qquad [4.7]$$

The coefficients of the equations regressed in Figure 4.4 were similar, even though 2013 had one erosive rainfall (Eq. [4.6]). Thus, the simple model to Eq.[4.2] for glyphosate decay in Chinese loess soil can be expressed as:

$$\frac{C_t}{C_0} = e^{-0.2\, t} \quad (p<0.01,\ R^2=0.93,\ \mathrm{n}=144) \qquad [4.8]$$

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. [4.8] were scattered and fitted well with the observed contents in 2012 and 2013 (Figure 4.5).

Accordingly, in the upper 2 cm soil, AMPA content peaked on the third day after glyphosate application (Figure 4.6). 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.

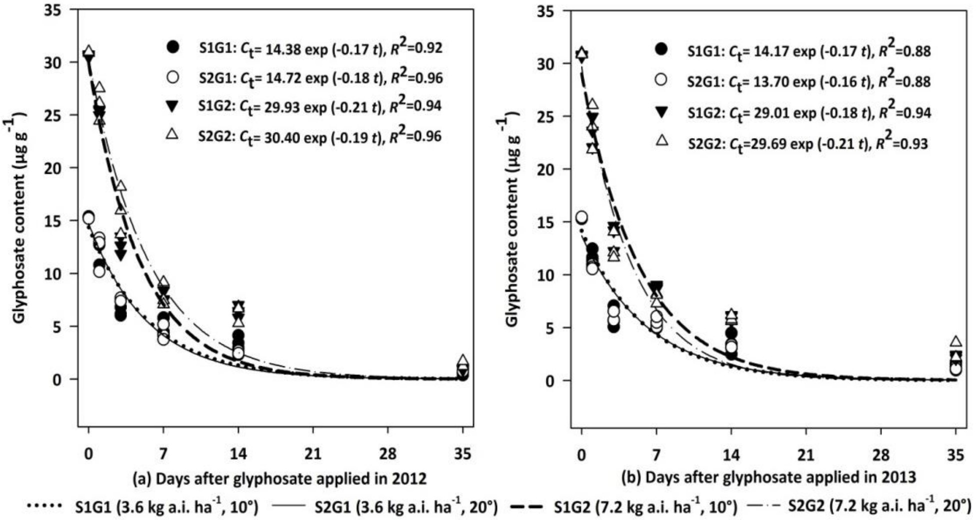


Figure 4.3 *Glyphosate content in upper 2 cm soil at the first 35 d after application in different treatments: (a) 2012; (b) 2013*

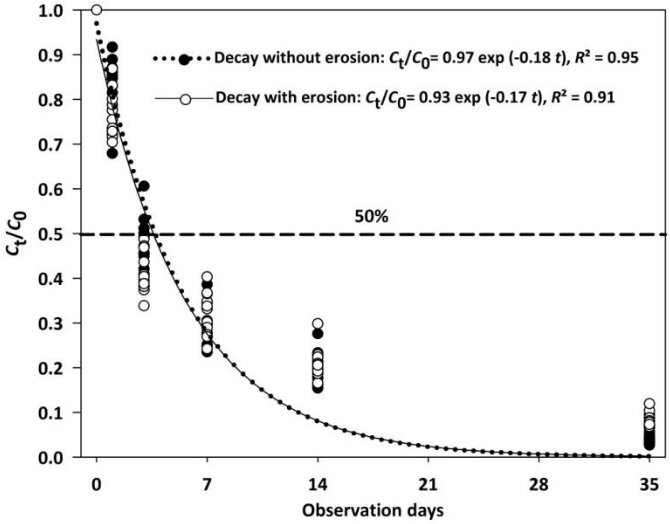


Figure 4.4 *The rate of glyphosate residues (C_t / C_0) in upper 2 cm soil during 35 days*

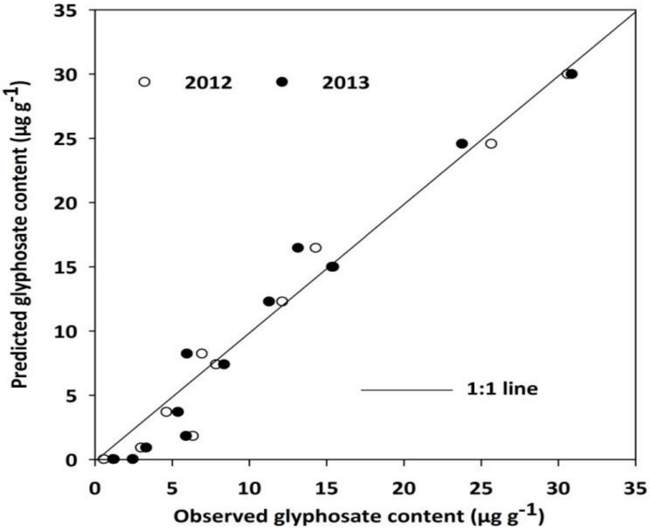


Figure 4.5 *Predicted (Eq. 4.8) vs. observed glyphosate content in upper 2 cm soil*

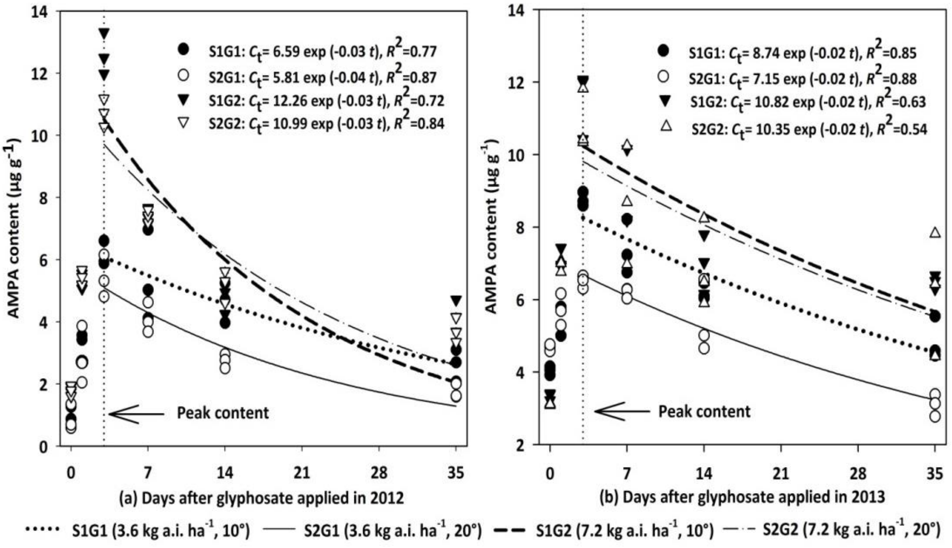


Figure 4.6 *AMPA content in upper 2 cm soil at the first 35 d after glyphosate application in different treatments: (a) 2012; (b) 2013*

4.3.3 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 0.38×10^{-4} L ha^{-1} and from 0.015 to 0.025×10^{-4} 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 μg mL^{-1} in the runoff and 40.44, 35.21, 71.85, and 58.95 μg 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 Eq. [4.4] and [4.5] 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±3 L kg^{-1} for glyphosate and AMPA, respectively. During soil erosion, most of the glyphosate was thus transported bound to soil particles rather than by dispersion in the runoff (Table 4.4).

Table 4.4 *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* (kg ha^{-1})	0.011	0.017	0.023	0.026
Transport rate (%)	0.31	0.46	0.32	0.37

* The amount of AMPA was calculated as parent glyphosate according to molecular mass;
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°).

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 4.2 and 4.3). 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 is similar in different two years but further work is needed to verify the factors on glyphosate decay in loess soil. 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. [4.8]), fitting with the first-order of chemical decay, in accordance with other studies (Bergström et al., 2011; Simonsen et al., 2008). The coefficient k in our study (Eq. [4.8]), however, were 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 (Figure 4.5).

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 (Bergström 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 (Lanctot 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 (Bergström 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., 2004a). 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; Bergström 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 g m^{-2} 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., 2011b). Therefore, further study is needed for monitoring glyphosate/AMPA on-site and off-site in this loss soil area under multiple scenarios (e.g. tillage, irrigation, and erosion control management) and glyphosate applications.

4.5 Conclusions

The rapid rate of glyphosate decay in Chinese loess soil indicates that the risks of on-site glyphosate pollution and leaching to deeper soil are low. Intense rains are an essential factor for the off-site 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 off-site risks involving decay processes.

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5 Integration of transport concepts for risk assessment of pesticide erosion

Environmental contamination by agrochemicals has been a large problem for decades. Pesticides are transported in runoff and remain attached to eroded soil particles, posing a risk to water and soil quality and human health. We have developed a parsimonious integrative model of pesticide displacement by runoff and erosion that explicitly accounts for water infiltration, erosion, runoff, and pesticide transport and degradation in soil. The conceptual framework was based on broadly accepted assumptions such as the convection-dispersion equation and lognormal distributions of soil properties associated with transport, sorption, degradation, and erosion. To illustrate the concept, a few assumptions are made with regard to runoff in relatively flat agricultural fields: dispersion is ignored and erosion is modelled by a functional relationship. A sensitivity analysis indicated that the total mass of pesticide associated with soil eroded by water scouring increased with slope, rain intensity, and water field capacity of the soil. The mass of transported pesticide decreased as the micro-topography of the soil surface became more distinct. The timing of pesticide spraying and rate of degradation before erosion negatively affected the total amount of transported pesticide. The mechanisms involved in pesticide displacement, such as runoff, infiltration, soil erosion, and pesticide transport and decay in the topsoil, were all explicitly accounted for, so the mathematical complexity of their description can be high, depending on the situation.

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5.1 Introduction

Pesticides are widely used in agriculture, horticulture, and forestry, and pesticide pollution has become an important issue worldwide (Damalas, 2009; Enserink et al., 2013). The high risks and long-term effects of pesticides on ecosystems have been studied for various components of the environment (Geissen et al., 2010; Ruiz-Suarez et al., 2014; Thomsen et al., 2014). Great efforts have been made to enhance pesticide monitoring and to reduce potential risks by adopting policies of pesticide use and its properties (EPA, 2003; Peeters et al., 2014) and by establishing a desired level of environmental quality (Horst et al., 2014; Rousseau et al., 2012; Valk et al., 2014).

Pesticides applied to fields are generally taken up by plants, adsorbed by soil particles, or volatilised into the atmosphere. Pesticides directly or indirectly enter soils with rainwater and/or from the root system (Köhne et al., 2009; Passeport et al., 2013) and become subject to soil physicochemical processes, such as infiltration, transport, sorption, decay, accumulation, and mineralisation by microbial activities (Beyer et al., 2014; Jarvis, 2007; Riah et al., 2014; Watanabe and Takagi, 2000). Thus, the fate of pesticides in environmental systems is quite complex (Gassmann et al., 2014). European Union (EU) legislation provides rules to prevent and cure the chemical pollution of water: the selection and regulation of substances of EU-wide concern (the priority substances) and the selection of substances by individual member states of national or local concern (pollutants specific to river basins) for control at the relevant level (EC, 2012). As a general criterion, critical pesticide concentrations of 0.1 $\mu g\ L^{-1}$ have been defined as admissible in drinking water in the EU. With increasing pesticide use, pesticide occurrence is high, and some pesticides have been banned for years (Zhong et al., 2014). Many studies have been conducted on the dispersion of pesticides and their accumulation and translocation in water, soil, and plants, but identifying their source is difficult due to the qualification and quantification of hundreds of compounds with different physicochemical properties in different climatic conditions (Parween et al., 2014; Steffens et al., 2014).

Pesticide transport in soil has two important paths: vertical leaching and horizontal washing. Both are involved in water-soil interphase reactions associated with pesticide degradation and ad/desorption. To assess the risks of pesticide leaching, mathematical models have been proposed (Styczen et al., 2011a), such as the one-dimensional MACRO (Jarvis et al., 1994) and PRZM_GW model (Carsel et al., 1985). Other leaching models such as LEACHM (Hutson et al., 1989), PLM (Nicholls et al., 2000), PEARL(Leistra et al., 2001), and GeoPEARL (Tiktak et al., 2002) have been developed either based on principles of chemical dispersion or drawing on advanced technology. Surface runoff is another important mechanism for pesticide transport, especially in highly erodible areas. Heavy rains can move pesticides both in the runoff water and attached to eroded soil particles (Majewski et al., 2014). This displacement may adversely affect ponds, lakes, rivers, and aquatic ecosystems in general (Blann et al., 2009). Models have been developed to simulate pesticide transport with surface water, such as ARM (Donigian and Davis, 1978), CREAMS (Knisel, 1980), ANSWERS (Dillaha III and Beasley, 1983), AGNPS (Young et al., 1986), RZWQM (Ahuja et al., 2000), and PeLM (Chen et al., 2004). These models for assessing the risks of pesticides mainly focus on the dissolved portion, and the pesticides absorbed on particulate particles have rarely been characterised (McGechan and Lewis, 2002).

In the present paper we quantify pesticide transport in soil, taking a first-order decay into account, by integrating models of runoff and erosion with variable rates of infiltration and sorption. The duration of pesticide decay before erosion and degradation rate was also included in the developed model. Basic model concepts and algorithms to verify pesticide transport associated with these processes are tested and discussed based on the performance of the selected reference output values.

5.2 Theory and governing equations

Pesticides applied to the soil surface that bypass the foliage are transported to deeper soil layers by infiltrating rainwater. Water ponding and surface runoff by Hortonian or Dunne overland flow can occur under certain circumstances, e.g. if rainfall exceeds the infiltration capacity of the soil or if the soil contains a low amount of stored water, which may induce soil erosion and pesticide displacement, either dissolved in runoff or entrained with the eroded soil. The quantity of pesticide actually moved to the surface water or depressions on the soil surface therefore depends on the amounts of runoff, erosion, and pesticide in the eroded soil. The latter in turn depends on the depth to which the pesticide has penetrated into the soil and how much of it has degraded.

5.2.1 Runoff and infiltration

Surface runoff occurs if the soil is saturated and its capacity to store infiltrating water has become depleted, but it occurs also if rain intensity exceeds the hydraulic conductivity of the soil. Surface runoff or overland flow are complex processes, and modelling can be highly demanding on the data and computational power (Van der Ploeg et al., 2012). Concerning runoff and erosion strongly depending on local micro- and mesotopogrophy but not only on “global” hillslope, we have chosen to parsimoniously model a relatively flat agricultural terrain. The runoff rate could thus be expressed as a functional relationship among precipitation rate, infiltration rate, and surface-soil roughness. Rearranging the terms of the equation presented by Appels et al. (2011) yields:

$$\frac{r(t)}{p(t)} = \left(1 - \frac{i(t)}{p(t)}\right) . f\left[\frac{P-I}{DSC}\right] \qquad [5.1]$$

which can be rewritten as:

$$r(t) = p(t)\left(1 - \frac{i(t)}{p(t)}\right) . f\left[\frac{P-I}{DSC}\right] \qquad [5.2]$$

where *t* is the rainfall time (min), $r(t)$ is the runoff rate (m min^{-1}), $p(t)$ is the precipitation rate (m min^{-1}), $i(t)$ the infiltration rate (m min^{-1}), *P* is the cumulative precipitation (m^3), *I* is the cumulative infiltration (m^3), and *DSC* is the storage capacity of depressions (m^3), where the latter three may be expressed per m^2. In these equations, precipitation (either as a cumulative value or as a rate) is a forcing function that is derived from observations or climatic data. Eq. [5.2] is based on the assumption of a fill-and-spill mechanism for surface depressions that overflow, with an instantaneous redistribution of runoff water in a unit area (m^2). A more dynamic modelling of runoff has been described by Yang and Chu (2015). Their method is computationally much more demanding, and produces similar results to those by Appels et al. (2011). Therefore, it was decided to use Eq. [5.1]-[5.2].

The function *f*[] in Eq. [5.2] depends on the micro-, meso-, and macro-topographical features of the soil and is often sigmoid. The logistic function is a suitable and flexible function that captures experimental forms well:

$$f[x] = \frac{1}{(1+ae^{-bx})} \qquad [5.3]$$

where a and b are dimensionless parameters, and $x = (P - I)/DSC$.

The value of *DSC* is governed by the roughness of the soil surface, which in turn depends on the presence of soil aggregates (at small or local topographical scales), tillage meso-structure, and the (macroscopic or global) slope of the field. We corrected the DSC-value for slope based on our observations and those by R. Barneveld [Bioforsk, Aas, Norway, pers. comm. 2014] according to:

$$DSC(S) = DSC(0) \cdot e^{\alpha S} \qquad [5.4]$$

where S is the slope of the terrain (°), and α is a coefficient ($°^{-1}$) .

The influence of the local topography on the value of *DSC* can be described as a linear relationship (Appels et al., 2011):

$$DSC(0) = k \cdot \sigma \qquad [5.5]$$

where k is a linear coefficient (m^2), and σ is the standard deviation of the soil-surface level (m) that could be quantified with, for example, laser technology (Barneveld et al., 2013). The parameters of Eqs. [5.3-5.5] were fitted to the results by Appels et al. (2011), a=128, b=5, α =0.023, respectively, and k in Eq. [5.6] was derived from unpublished data (k=0.17) of Barneveld.

Eqs. [5.1-5.2] indicate that runoff also depends on infiltration. Infiltration rates depend on soil porosity, initial soil moisture (θ_i), and soil texture and structure (Sharma et al., 1980). A lot of computer programmes are available to model infiltration into soils, either with or without ponding. These programmes usually require detailed information on the upper boundary (ponding water depth, or no ponding) in addition to various soil and canopy properties. Computational demands are modest for one-dimensional modelling, but a simpler approach will be sufficient to test our concept. Therefor we choose the Philip (1957) model, which is a relatively simple way to approximate the infiltration rate:

$$i(t) = \frac{S_s}{2\sqrt{t}} + K \qquad [5.6]$$

where S_s is the sorptivity (m $min^{-1/2}$) and K is the hydraulic conductivity (m min^{-1}). The sorptivity affects the infiltration rate mainly at the short term for relatively dry, fine-textured soils. Longer term infiltration rates mainly depend on the hydraulic conductivity. Macropore flow may also need to be included, depending on the infiltration conditions and the soil type. The effects of sorptivity and hydraulic conductivity could be expected to be (inversely) correlated through soil types, but no significant relationship has been found between S_s and K (Haghighi-Fashi et al., 2014; Stewart et al., 2013). The effects of the sorptivity on the infiltration rate decrease during a rainfall event and are particularly important on very dry soil (with all its complications of wettability) and significantly complicates infiltration because initial wetness should be known at the beginning of each rainfall event, so we complied with Yang and Chu (2015) by using a Green-Ampt infiltration model with S_s=0. We translated the infiltration rate into a pore water velocity (see below) by assuming that most infiltration occurs when the soil volumetric water fraction exceeds the moisture content at field capacity (θ_{fc}) but decreases rapidly when the moisture content is smaller. Assuming that all resident soil water is pushed downwards by the infiltrating water (Wierenga, 1977), the infiltration front will be at a depth equal to the cumulative amount of infiltrated water, $I(t)$, divided by θ_{fc}.

5.2.2 Soil loss and eroded depth

Raindrop-induced soil detachment, sediment transport, and deposition occur simultaneously during erosion. Physically based models are essential for predicting erosion by overland flow in different scenarios. The capacity of sediment transport in such models is commonly the maximum equilibrium sediment load that can be carried overland under the particular rate of runoff discharge flow (Foster and Meyer, 1972). Sediment-transport capacity, including flow regions (laminar or turbulent), can be represented by piecewise functions (Beasley et al., 1980):

$$T_c = 146\, S_c q^{0.5} \quad (q \leq 0.046) \qquad [5.7]$$

$$T_c = 14600\, S_c q^{2} \quad (q > 0.046) \qquad [5.8]$$

where T_c is the sediment-transport capacity (kg m^{-1} min^{-1}), S_c is the tangent slope gradient (m m^{-1}), and q is the flow rate across the width of the slope (m^3 m^{-1} min^{-1}). A general approximation of the sediment-transport capacity has been given by (Govers, 1990) who describes it as a function of discharge and slope. The relationship was based on a series of laboratory experiments with a hydraulic flume and was presented as

$$T_c = A_c \cdot S_c^B \cdot q^C \qquad [5.9]$$

where A_c, B, and C are dimensionless coefficients associated with grain size and with laminar and turbulent-flow regimes, respectively. The values of $1.0 \leq B \leq 1.8$ and $0.9 \leq C \leq 1.8$ are recommended for modelling sediment transport, especially the median of each parameter ($B = C = 1.4$) (Prosser and Rustomji, 2000). Some studies have validated Eq. 8

(Julien and Simons, 1985; Prosser and Rustomji, 2000; Wang et al., 2015b; Zhang et al., 2009), but the coefficients for the slope and discharge are still within the above ranges. Therefore, in present study, we supposed to use Eq. [5.7] to calculate sediment-transport capacity and then the results were used as a base to compute pesticide residues. Two main types of erosion be distinguished:

i. sheet erosion: eroded surface area is equal to the total area A ($\gamma=1$)
ii. gulley erosion: eroded surface area is γA, with $0<\gamma<1$

where A is the eroded area (m^2) and γ is the dimensionless eroded fraction. Then $q(t)$ is given by:

$$q(t) = A \cdot \gamma \cdot r(t)/w \tag{5.10}$$

where w is the width of the runoff channel (m). Combining Eqs. [5.2], [5.7], and [5.10] and the duration of the rain (t, min), the total amount of soil loss M (kg) can be obtained if S_c and q are known. Now the eroded soil volume V (m^3) can be obtained from

$$V = \frac{M}{\rho} = \frac{\sum_{i=1}^{N_t} T_C \cdot \Delta t_i \cdot w}{\rho} = \frac{\sum_{i=1}^{N_t} 146 \cdot S_C \cdot \left\{\frac{A \cdot \gamma \cdot r(t)}{w}\right\}^{0.5} \cdot \Delta t_i \cdot w}{\rho} \tag{5.11}$$

where Δt_i is the i^{th} time interval (min) (i=0, 1, ... , N_t), N_t is the number of discrete time intervals the rainfall event lasts (if we assume an interval size of 1 minute, then N_t will be equal to the number of minutes. and ρ is the bulk density of the soil (kg m^{-3}). We assume that a soil layer with thickness Δz (m) will be eroded by overland flow. Δz can then be calculated as:

$$\Delta z = \frac{V}{\gamma A} = \frac{\sum_{i=1}^{N_t} 146 \cdot S_C \cdot \left\{\frac{A \cdot \gamma \cdot r(t)}{w}\right\}^{0.5} \cdot \Delta t_i \cdot w}{\rho \cdot \gamma \cdot A} \tag{5.12}$$

5.2.3 Pesticide fate in soil

Pesticides are generally sprayed incidentally on soil and vegetation. Ignoring the pesticide that is directly taken up by the vegetation, spraying can be approximated as an instantaneous application of a designated quantity at the soil surface. After spraying, rainwater infiltrates, and the pesticide will be transported to deeper into the soil. Common assumptions (FOCUS, 2014) are a homogeneous topsoil, linear ad/desorption and first-order decay, yielding the mass balance equation:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial z} - \mu RC \quad [5.13]$$

where C is the concentration of the pesticide in the soil water (mg m^{-3} water), z is the depth of pesticide infiltration (m), t is the time for water infiltration (min), v is the pore water velocity (m min^{-1}) that follows from cumulative infiltration and θ_{fc}, μ is the degradation coefficient (min^{-1}), D is the coefficient of dispersion (m^2 min^{-1}) and R is a retardation factor (Jury and Gruber, 1989) given by:

$$R = 1 + \frac{\rho}{\theta}K_d \quad [5.14]$$

and the distribution coefficient, K_d (m^3 kg^{-1}), is given by:

$$K_d = \frac{dS_a}{dC} \quad [5.15]$$

K_d is assumed to be proportional to the organic matter fraction ($K_d = f_{om} \cdot K_{om}$, where K_{om} is the organic matter fraction corrected adsorption coefficient, m^3 kg^{-1}; the mass fraction f_{om}, of organic matter, is often spatially variable). Pesticides are present in relatively small concentrations, do not affect the sorption of each other, and can be modelled separately.

Eq. [5.13] can be solved analytically for many initial and boundary conditions. Numerical approximations are usually needed when initial and boundary conditions vary spatiotemporally. It was considered that, in a first approximation, hydrodynamic dispersion can often be regarded as a secondary effect in comparison with larger scale horizontal spatial variability of solute transport (Destouni and Cvetkovic, 1991). We thus ignored pore-scale dispersion (setting D=0) in a first approach, and Eq. [5.13] then shows that the pesticide present at t=0 at a certain depth ($z_{c[t=0]}$) could, after a time t, be found a depth given by:

$$z_c(t) = \frac{vt}{R} + z_{c[t=0]} \quad [5.16]$$

The last term in Eq. [5.16] indicates that the pesticide at time t=0 can have infiltrated into the soil already. Then this depth will be spatially variable due to the spatial variability of, in particular, the soil hydraulic properties, sorption distribution ratio (often proportional to the strongly varying fractions of soil organic matter and clay), and cumulative infiltration. The values of v and R are assumed to be lognormally distributed, so depth z_c has a lognormal distribution as well and $\ln(z_c)$ is distributed normally (Van Der Zee and Van

Riemsdijk, 1987). If the mean and variance of v and R, or of their logarithmic transformations, is known, those of the depth to where the pesticide has infiltrated can be easily calculated.

The cumulative infiltrated amount, I, in Eq. [5.6] can be calculated for each time under consideration. Neglecting sorptivity (S_s=0) and assuming the hydraulic conductivity K to be constant, then $v = K/\theta_{fc}$ and $I=K\cdot t$. We postulated that all resident water in the soil at the beginning of a rain is pushed downwards by the infiltrating water of the rain. The freshly infiltrated water will then reach the depth (Δz_w, m):

$$\Delta z_w = [K/\theta_{fc}] \cdot t = v \cdot t = I/\theta_{fc} \qquad [5.17]$$

The average pesticide depth will be:

$$\Delta z_c = \frac{\Delta z_w}{R} + z_{c[t=0]} \qquad [5.18]$$

Due to the spatial variability of v, R, and $z_{c[t=0]}$ in this model, pesticide is found at different depth throughout the area. For simplicity, as often pesticide is sprayed under dry conditions, at the onset of rainfall we can assume that the initial depth of the pesticide was zero. If the pesticide has been sprayed on the soil uniformly, the mass of soil that still contains pesticide depends on the part of the terrain where the pesticide depth has not yet exceeded the thickness of the eroded soil layer Δz. Because the depth of pesticide is lognormally distributed, the fraction of the terrain ($f_{A,P}$) where soil containing pesticide is eroded is equal to the probability that $z_c<\Delta z$ for an area A given by Van Der Zee and Van Riemsdijk (1987). This fraction is given by:

$$f_{A,P} = Pr\{z_c \leq \Delta z\} = 1 - \frac{1}{2} erfc\left[\frac{\ln(\Delta z) - m_{lnz}}{\sqrt{2} s_{lnz}}\right] \qquad [5.19]$$

with

$$m_{lnz} = m_{lnv} + \ln(t) - m_{lnR} \qquad [5.20]$$

and

$$s_{lnz}^2 = s_{lnv}^2 + s_{lnR}^2 \qquad [5.21]$$

Where

$$erfc\ (x) = \frac{2}{\pi^{\frac{1}{2}}} \int_{x}^{\infty} \exp(-x^2)\, dx \qquad [5.22]$$

and m_{lnz}, m_{lnv}, m_{lnR}, S_{lnz}, S_{lnv}, and S_{lnR} are the means and standard deviations of lognormally distributed lnz, ln*v*, and ln*R*, respectively.

5.2.4 Pesticide mass in eroded soil

If soil is eroded only from a part (γ) of the area and only a part of that soil ($f_{A,P}$) contains pesticide, these two fractions must be multiplied to obtain the fraction of soil area from where the pesticide erodes. If it initially contained pesticide from an application m_0 (kg m^{-2}), then the total mass *m* (kg m^{-2}) of eroded (and runoff) pesticide is equal to the quantity that did not degrade (with rate constant μ) in the time t_a (min) that elapsed since the application. The mass of undegraded pesticide eroded from the total area (*A*), corrected for the fractions γ and $f_{A,P}$, is given by:

$$m = m_0 \cdot e^{-\mu R t_a} \cdot A \cdot \gamma \cdot Pr\{z_c \leq \Delta z\} \qquad [5.23]$$

We complied with the EU pesticide-screening policies and models where both dissolved and adsorbed pesticide are subject to transformation (FOCUS, 2000). If we assume that only dissolved pesticide is transformed in soil, in lieu of the discussion in the literature regarding bio-availability and bio-accessibility of organic contaminants, Eq. [5.23] should be adjusted by deleting *R* in the exponential term (Beltman et al., 2008). Substituting Eq. [5.12] in Eq. [5.23] thus produces an equation containing the total mass, *m*, of eroded pesticide:

$$m = m_0 \cdot e^{-\mu R t_a} \cdot A \cdot \gamma \cdot Pr\left\{ z_c \leq \frac{\sum_i^t 146 \cdot S_c \cdot \left\{\frac{A \cdot \gamma \cdot r(t)}{w}\right\}^{0.5} \cdot t_i \cdot w}{\rho \cdot \gamma \cdot A} \right\} \qquad [5.24]$$

5.2.5 Sensitivity and model parameterisation

The parameters in this model for the various processes of pesticide transport associated with erosion may affect the mass *m* in different ways, some straightforward and others complex. We conducted a sensitivity analysis to determine the influence of a set of parameters on predicting runoff, soil loss, depth of soil layers with pesticide, and pesticide residues in soils. Sensitivity was determined using the relative sensitivity function (Boekhold and Van der Zee, 1991), *U*, for the system y= *f* (y, x, t) defined as:

$$U_y(x) = \frac{\partial y(x,t)}{\partial x} \cdot \frac{x}{y(x,t)} = \frac{\partial \ln(y(x,t))}{\partial \ln(x)} \qquad [5.25]$$

Values of U_y(x) ranging from - 1 to 1 indicate the attenuation of x in y, and values <-1 or >1 imply that variations in x are amplified in y. Negative values of U_y indicate a decrease in y when x increases.

The linkage between the total amount of eroded pesticide and T_c in Eq. [5.21] involves slope, runoff, and roughness of the soil surface. Eq. [5.7] was selected to assess total soil loss during erosion. The relative sensitivity functions for the related parameters *S*, σ, and θ_{fc} can thus be derived.

Model sensitivity depends on the reference situation, i.e. the combination of parameters involved, so a consistent set of parameter values must be used. The soil infiltration rate is important for the runoff and therefore also for the thin layer of eroded soil. It was estimated based on the saturated hydraulic conductivity (K_s). We used published data for saturated hydraulic conductivity (Saxton and Rawls, 2006). We used a first-order model for pesticide decay in soil:

$$m_t = m_0 e^{-\mu t_a} \qquad [5.26]$$

with a half-life time DT_{50} (d) of

$$DT_{50} = \frac{ln2}{24 \cdot 60 \cdot \mu} \qquad [5.27]$$

We then set μ=8.0×10^{-6}, with an approximate half-life of 60 d, for pesticide decay in soil. The variation of *v* can be set at 20% of the velocity calculated by k/θ_{fc}. The values for the other parameters are shown in Table 5.1.

Table 5.1 *Parameter values used in calculations*

Parameter	Description	Value
σ	Standard deviation of soil surface level (m)	0.2
$K_s{}^{\#}$	Saturated hydraulic conductivity (m min^{-1})	3.67×10^{-4}
$\theta_{fc}{}^{\#}$	Field capacity (-)	0.3
K_d	The sorption coefficient of pesticide to soil (m^3 kg^{-1})	0
I_0	Cumulative infiltration from pesticide applied to erosion rainfall (m^3)	0.001
R^{ξ}	Retardation factor (-)	$\Lambda(1, 0.1)$
p	Precipitation rate (m min^{-1})	1.5×10^{-3}
t	Rainfall duration causing erosion (min)	60
t_a	Time for pesticide decay before erosion rainfall (min)	20160
ρ	Soil bulk density, kg m^{-3}	1200
μ	Decay rate coefficient (min^{-1})	8.0×10^{-6}
m_0	Initially applied pesticide (kg m^{-2})	1.0
γ	Eroded fraction (-)	1
w	The width of runoff channel (m)	1.0

means data from Saxton and Rawls (2006); * the retardation factor is lognormally distributed $\Lambda(\mathrm{m_{lnR}}, \mathrm{S^2_{lnR}})$ and defined by mean of lnR ($= \mathrm{m_{lnR}}$) and its standard deviation ($= \mathrm{s^2_{lnR}}$).

5.3 Results and discussion

The runoff rate and soil loss were calculated for various slopes (5, 7.5, 10, 12.5, and 15°) using the input parameters of the model (Figure 5.1). Runoff rates calculated according to Eq. [5.2] increased rapidly with slope and then reached a maximum value (Figure. 5.1a). Runoff rates varied with slope at the beginning of the rainfall event due to the predominate effect of micro-depressions and converged at the same level when constant infiltration was balanced by the simulated rain intensity. Concerning the eroded area and erosion type, the sediment-transport capacity calculated by Eq. [5.7] accordingly varied with rain duration. Due to the variation of runoff, soil sediment transport capacity differs significantly (Figure 5.1b).

Both the total mass of soil loss M and the eroded soil depth Δz can be calculated using the values of runoff and sediment-transport capacity. Determining the pesticide distribution and its mass in such eroded soil layers requires information of the depth of pesticide infiltration. The total cumulative infiltration should include all the infiltration in the soil after the application of the pesticide. Thus, the total cumulative infiltration TCI is the sum of I_0 (cumulative infiltration from pesticide applied to erosion occurring) and I_{60} (total cumulative infiltration within 60 min of erosion by rainwater). The average depth of soil containing pesticide thickness of the soil layer Δz_c (Eq. [5.18]) that contains pesticide, the

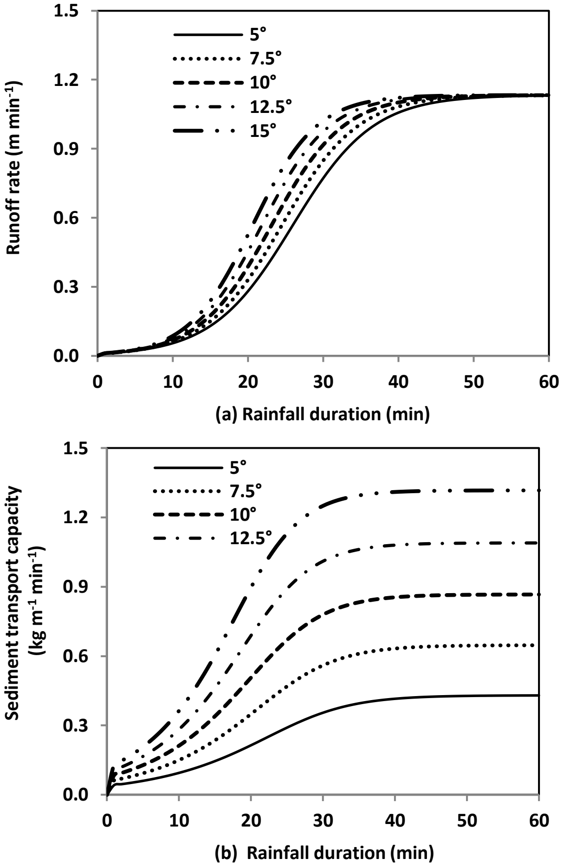

Figure 5.1 *Temporal variations of runoff rate (eq.[5.2]) and sediment transport capacity (eq.[5.7])*

Table 5.2 *The mass of transported pesticide*

Slopes (°)	Δz (m)	TCI	Δz_c (m)	PDP (-)	*m* (kg m^{-2})
5	0.015	0.023	0.077	0.84	0.7407
7.5	0.023	0.023	0.077	0.87	0.7626
10	0.031	0.023	0.077	0.89	0.7764
12.5	0.040	0.023	0.077	0.91	0.7862
15	0.049	0.023	0.077	0.92	0.7936

Δz is the eroded soil depth, m;

TCI is the total cumulative infiltration, m^3;

Δzc is the average depth of soil containing pesticide, m;

PDP is the probability that pesticide is in the eroded layer;

probability that pesticide is in eroded soil and the total mass of transported pesticide (*m*) can then be calculated by the Eqs. [5.18-5.24] (Table 5.2). The results show that the depth of eroded soil increases with slope. Therefore the probability to find pesticide in the eroded layer also increased, leading to more transported pesticide at higher slopes.

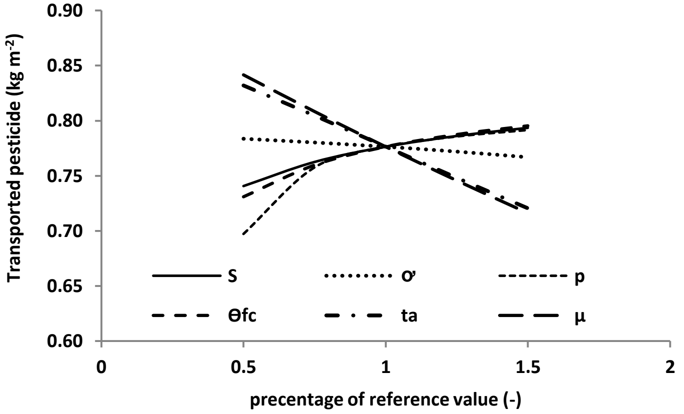

Figure 5.2 *Comparison of erosion-transport of pesticide mass, m, as a function of six varied parameters relative to their reference values. Calculations based on Eq. [5.24] with initially applied a real pesticide mass equal to* m_0*=1.0 kg* m^{-2}*, and reference parameter values: S=10°, σ =0.2 m, p=0.0015 m* min^{-1}*,* θ_{fc}*=0.3,* t_a*=20160 min, and μ=8.0 ×10-6* min^{-1}*. Parameters ranging from 50% to 150% of reference values.*

We selected some parameters to test the behaviour of the model in various scenarios. The parameter reference values were a slope of 10°, deviation of soil-surface level σ of 0.2 m, rain intensity p of 0.0015 m min^{-1}, field capacity θ_{fc} of 0.15, duration of pesticide decay before erosion by rainwater ta of 20160 min (14 d), and a decay rate μ of 8.0×10^{-6} min^{-1}. The calculations were based on ranges of the reference values from 50 to 150% (Figure 5.2). As could be expected, the mass of transported pesticide increases with slope, rain intensity, and field capacity. Eqs. [5.7-5.8] indicate that sediment-transport capacity depends on slope and discharge, which are depending on rain intensity and infiltration. The aerially averaged infiltration rate is constant in this model, so soil loss has been determined by slope and rain intensity. Many studies have been presented regarding the relationship between erosion rate, slope and discharge. Pore water velocity in soil depends on the moisture content at field capacity (Eq.5.17), so travelled distance will be small for high values of the moisture content at field capacity. Most of the pesticide will then remain in a very thin layer of soil just below the surface, which is easily eroded. The mass of transported pesticide decreases with increasing roughness (σ; Eq.[5.5]) of the soil-surface level (leading to less runoff), the duration of pesticide degradation before erosion by rainwater and the degradation rate, implying that the time of pesticide application and the half-life should be taken into account to reduce the risks of pesticide transport offsite. The pesticide will not have enough time to decay if a heavy erosional rain falls shortly after application, which represents a high risk of pesticide transport by processes associated with erosion.

As Figure 5.2 reveals, the response of pesticide export on the varied parameters is approximately linear in most cases. However, the entire model is distinctly nonlinear in character, as is also shown in e.g. Figure 5.1. This nonlinearity can be recognized in Figure 5.2 from the line related with variation of the precipitation rate *p*, that shows an increasing slope as this rate decreases. Similarly, nonlinearities could be expected in relation with e.g. degradation rate, which is exponential in character due to the first order rate equation. It is one of the benefits of the developed model, that for different reference cases, it is possible to identify which nonlinearities become apparent, and which are overruled by the impact of other model parameters.

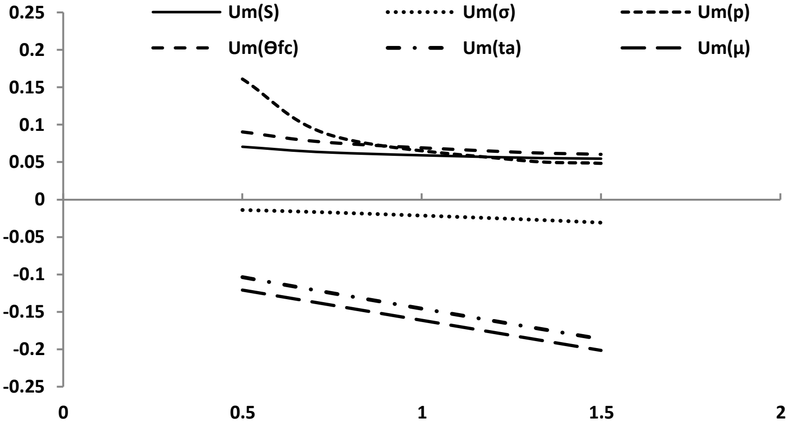

Figure 5.3 *The relative sensitivity, U, of pesticide transport as mediated by erosion (Eq.[5.25]) as a function of 6 parameter values relative to their reference value.*

Figure 5.3 shows the relative sensitivity, *U*, of the model output parameters to changes in slope S, deviation of soil-surface level σ, rain intensity *p*, field capacity θ_{fc}, duration of pesticide decay before erosion by rainwater t_a, and degradation rate μ. The sensitivity of the model to changes in *S*, σ, and *p* is associated with models of soil-surface runoff and soil loss. $U_m(S)$ and $U_m(p)$ are positive but decrease as *S* and *p* increase, respectively. This implies that the total mass of pesticide transported with eroded soil increases with increasing S and p. With increasing values, the decreasing sensitivities indicate that the impact of those changes become less profound. In other words, these decreasing sensitivities emphasize the slightly nonlinear form of the lines in Figure 5.2. $U_m(\sigma)$ is negative, indicating that the mass of transported pesticide decreases with increasing the roughness of the soil surface. Model parameter θ_{fc} incorporates sorption and water status and reflects solute mobility. Water velocity and wetting depth are determined in our model by θ_{fc}. The sensitivity of the pesticide that is exported by erosion to variation in θ_{fc} is positive, and as discussed in relation with Figure 5.2, this is the effect of diminishing wetting depth. However, the water content also affects the retardation factor, which decreases as the water content increases. This would lead to enhanced erosion risk, as the pesticide would be less retarded with increasing water content, and move deeper. The numerical results therefore show that this latter impact is less than the impact through wetting depth. A high θ_{fc} , corresponding with soil structure, texture, and organic matter, results in a lower depth of the wetting front. Therefore, the major part of an applied pesticide cannot move to deeper soil and remains in the surface soil, which will be eroded if a heavy rain falls soon after application.

As the sensitivity $U_m(\theta_{fc})$ decreases towards zero if θ_{fc} is higher, we may conclude that the two effects (wetness depth and retardation) of the water content become more in balance at higher moisture. These dependencies depend of course on the value of the retardation factor: if R is large, the term of one in Eq.[5.14] becomes less significant and the sensitivity to water content should go to zero. Parameters ta and μ are associated with pesticide degradation. $U_m(t_a)$ and $U_m(\mu)$ are negative, and reflect that increasing either parameter leads to more pesticide degradation before the erosion event occurs. It is also clear, that the negative values of the sensitivities are relatively large, hence the eroded pesticide is more sensitive to pesticide degradation, than to the other parameters. This can only imply, that relatively much of the originally applied pesticide is still found in the erode soil layer. As the values of eroded pesticide in Figure 5.2 reveal (values above one half of applied pesticide), this is definitely the case for the current situation. In this situation, the management of pesticide application in relation with the probability of significant showers and the degradation rate of pesticide in relation with shower frequency (or interval time) is important for a proper pesticide risk assessment in areas of high erosion. It may also be expected that assumptions with regard to the degradability of both dissolved and adsorbed pesticide (i.e., the bioavailability discussion) may become important. As Beltman et al. (2008) showed, which convention is chosen may affect the anticipated leached pesticide fraction significantly. In summary, the sensitivity graphs that were shown illustrate which parameter values, and their variabilities, of S, σ, p, and θ_{fc} in pesticide transport, are the most important to be taken into account. As these sensitivities change as parameter values change, e.g. considering different areas with heterogeneous soil and varied topography, or different pesticide properties, a model as presented here is beneficial for the proper anticipations.

5.4 Conclusions

A simple integrated model was developed to assess offsite pesticide transport that is facilitated by soil erosion. In this model, runoff was predicted based on the balance of input rainwater and infiltration, in relation with the water storage that occurs before actual runoff occurs. This storage is dependent on surface roughness and the slope of the area. Runoff was linked to erosion to estimate soil loss and the thickness of the eroded soil layer. The probability density distribution of the soil depth containing pesticide was derived by simplifying the convection-dispersion equation, and assuming a lognormal distribution of the infiltration rate and adsorption coefficient. Combined, these results determined whether or not the pesticide was still resident in the eroded soil. Next, we considered first-order degradation because it affects the mass of pesticide in the soil, that had not yet degraded at the moment of erosion. Combining these three results gave an implicit expression of the mass of pesticide transported associated with soil erosion.

We assumed a uniform soil profile and constant infiltration. The analytical and numerical results focussed on the mass of pesticide transported during soil erosion as a function of the slope, rain intensity, deviation of the soil-surface level, soil field capacity, degradation rate coefficient, and pesticide half-life time before the onset of erosion. The runoff rate was influenced by the slope and converged at a steady level when precipitation and infiltration were balanced. The mass of soil loss and the depth of erosion with the duration of rain accordingly varied with runoff and slope. The relationship between soil sediment-transport capacity and runoff remains complex because of the interactions among soil properties, slopes, and discharge. In addition, a constant input of rainwater infiltrated steadily in a physically homogeneous soil column, which would transport pesticides to deeper soil layers.

The response of the model to variations in the input parameters was analysed using a simple relative sensitivity analysis. More pesticide will be transported at higher slopes, rain intensities, and soil field capacities, and less pesticide will be transported as the standard deviation of soil-surface level, or roughness, degradation rate coefficient, and duration of decay before erosion increase. With the model, it can be detected which of the many nonlinearities of the model dominate the response. Such insights are useful in focussing pesticide erosion experimental investigations, which can be expensive. It is also possible, with relatively simple means, to bring in additional complications which have been recognized as important in transport and erosion. For instance, with the convenient OpenLisem windows interface, it is easy to combine the present model with LISEM (Jetten, 2002). Thus, more detail can be given to pesticide erosion risk insofar as the erosion process is concerned.

Acknowledgements

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6 Synthesis

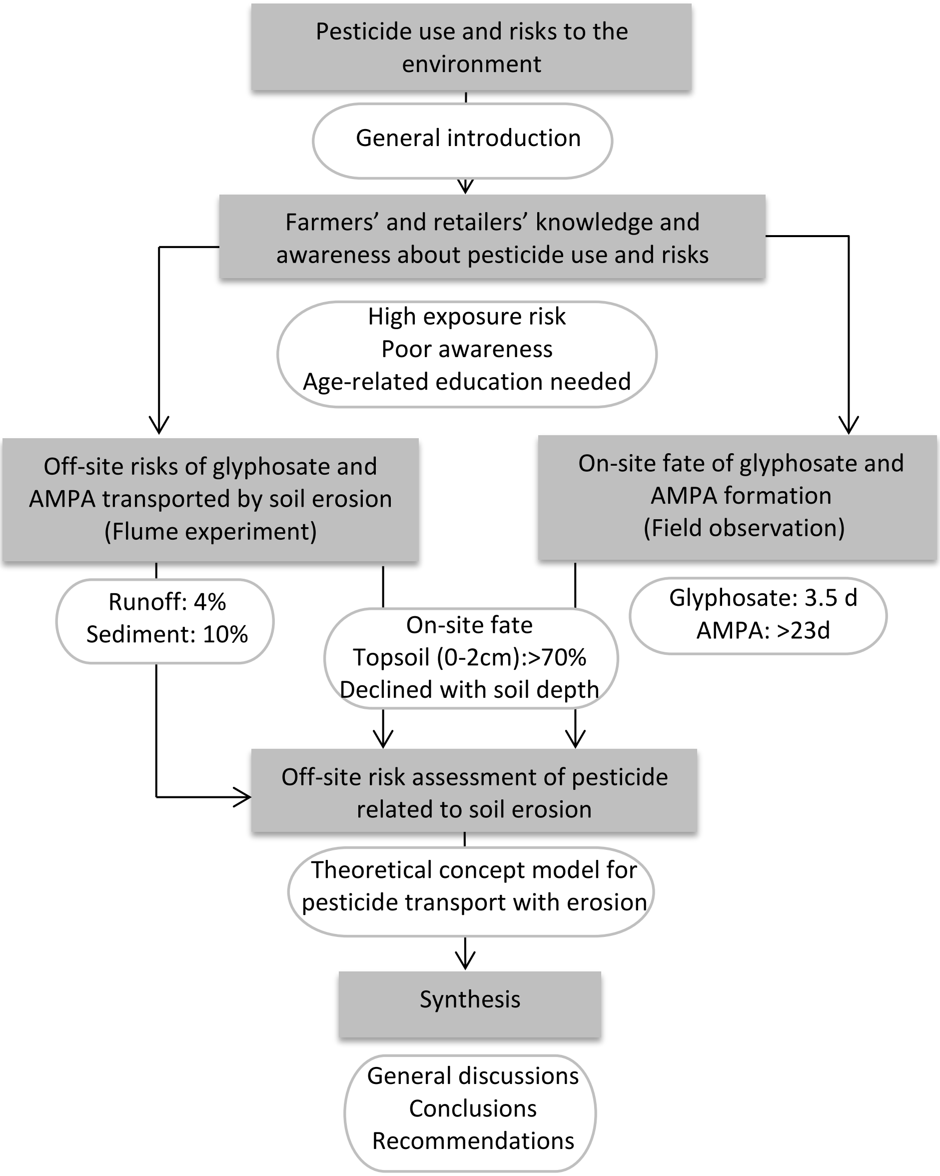

Figure 6.1 *The outline of this thesis with the objectives of learning about the farmers' perspectives on pesticide use the environmental fate of glyphosate and AMPA, and off-site risk assessment in the Wei River catchment. Based on the farmers' and retailers' survey (Chapter 2), the widely-used herbicide glyphosate was selected and its on-site and off-site risks were studied in a simulation rainfall lab (Chapter 3) and in a field observation station (Chapter 4). A theoretical concept model for pesticide particle-facilitated transport was developed (Chapter 5).*

6.1 General discussion

This thesis addressed four key objectives aimed at understanding farmers' knowledge and awareness about the risk of pesticide use, and the environmental fate and the off-site risk of the widely used herbicide glyphosate and its main metabolite AMPA. Here we synthesize the thesis research based on the results achieved and the objectives posed in the general introduction and depicted in Figure 6.1.

6.1.1 Farmers' and retailers' knowledge and awareness about pesticide use and risks in the Wei River catchment

The lack of knowledge and awareness of the risks of pesticide use were observed among farmers in the study regions (Chapter 2). The effects of this lack of knowledge and awareness on farmers' behaviour and health, along with their environmental risks, are summarized in Figure 6.1. As the end user of pesticides, a farmer's knowledge and awareness of pesticides significantly affects pesticide application (Matthews, 2008). Regarding the roles in a family, males do more physical work thus the gender-specific knowledge of pesticide use seems to be a precaution to the dangers of exposure (Atreya, 2007), especially for women living in rural regions (Cui, 2009; WHO, 2014). Due to the low education level of older farmers, they find it very difficult or impossible to understand the hazard warnings provided by the chemical industry and regulatory agencies (Ibitayo, 2006; Recena et al., 2006). Therefore, poisonings, exposure risks, and high mortality rates have been frequently reported (Phillips et al., 2002; Zhou et al., 2011; Zyoud et al., 2010).

Our findings showed that the protection and hygiene measurements taken for pesticide use were inadequate. Washing hands was the most commonly used mode of protection among farmers as opposed to wearing masks, showering, and changing clothes. This leads to a high level of pesticide exposure to the farmers themselves. Concerning the use of pesticides, correct application, proper protection, and good personal hygiene are considered to be good practices for the safe spraying of pesticides (Matthews, 2008). About 44.3% of pesticide poisoning could be avoided by using better protection measures (Dasgupta et al., 2007). Without these protection measures being taken, adverse symptoms (intoxication) such as cephalea, dizziness, vomiting, and skin problems have been reported after pesticide use (Ngowi et al., 2007a; Ngowi et al., 2007b; Recena et al., 2006; Yassin et al., 2002). Unfortunately, about 60% of the farmers surveyed had stored pesticides in their homes which increases the risks posed to drinking water, food and the health of children (Matthews, 2008; Salameh, 2004). Furthermore, the methods of storing and disposing of pesticide containers are an important aspect to consider when trying to reduce pesticide exposure in farming (Matthews, 2008). Similar to other studies (Hvistendahl, 2013; Ibitayo, 2006), surrounding soils, water and even human health are suffering from pesticide wastes. Additionally, some banned pesticides were still available indicating the lack of a functioning legislative framework in rural areas of China (Chen et al., 1998).

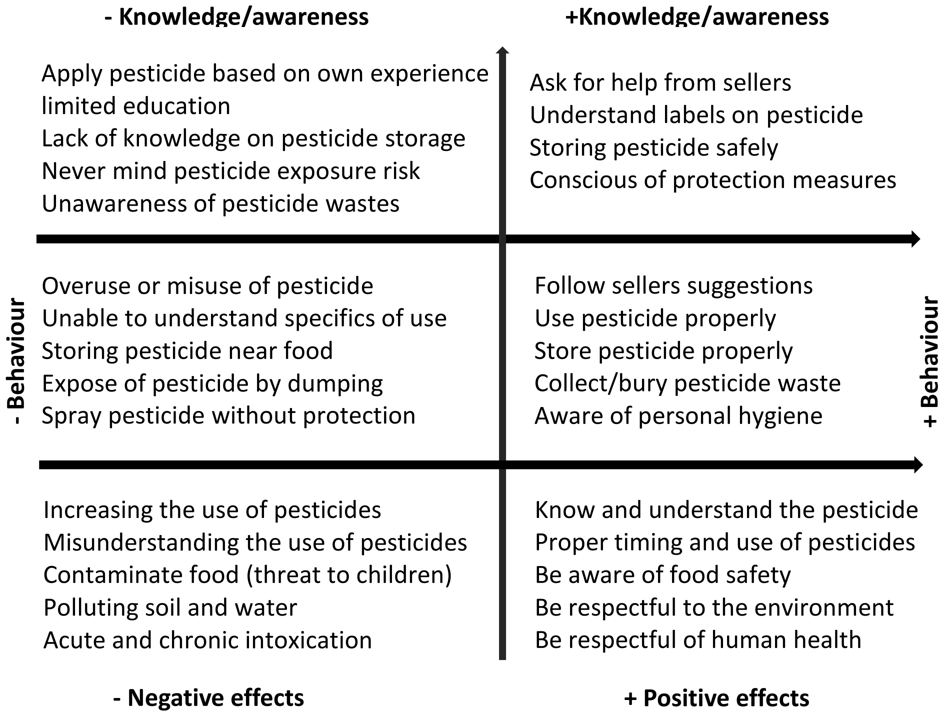

Figure 6.2 *Diagram of main findings about farmers' knowledge and awareness. Farmers' knowledge and behaviour are influenced by their education, experience and other people, such as neighbours and retailers. With better knowledge, farmers can use pesticides properly and safely resulting in positive effects on environmental systems and human health.*

The owners of local pesticide stores play an important role in pesticide use, often advising farmers and agricultural workers. This study is the first to focus on the sellers' roles in pesticide application in China. Impressively, most retailers provided guidance to farmers on the use of pesticides and on the protective measures available for their application. However, farmers were reluctant to adopt the recommended measures, preferring to rely on their own experience and the influence of their neighbours, such as shown in other studies (Matthews, 2008; Yassin et al., 2002; Zyoud et al., 2010).

In addition, the perception of risk is an important element in developing effective campaigns targeting education and communication (Damalas et al., 2008). Chen et al. (1998) reported that the prevalence of pesticide poisoning decreased significantly after farmers followed a safety education programme. Our findings suggest that educational programmes should be specifically focused on improving the self-protective consciousness of farmers when using pesticides, especially in the rural regions of developing countries. According to our survey, farmers had only some basic information about pesticide residues. The awareness of the dangers of pesticides to human health and environment varied depending on gender, age, educational experience, and even location. Pesticide management, however, is not only a concern for farmers but also for stakeholders, such as retailers, pesticide producers, and supervision authorities who can directly or indirectly affect farmers' behaviour (Fan et al., 2015). In order to get a better understanding of pesticide use in the study area, the survey will be upscaled in collaboration with multiple actors, such as farmers, agricultural advisors, local government staff, research institutions, pesticide distributors/retailers, among others. With the cooperation of these actors, current and promising pesticide management practices will be identified, documented and holistically assessed (i.e. regarding their economic, ecological and socio-cultural impact). This assessment will outline the criteria needed to select innovative practices or provide the basis to develop integrated ideas for management improvements (FAO, 2013).

6.1.2 Off-site transport of glyphosate and AMPA by runoff and erosion in Chinese loess soil

Based on the results of the survey, we chose to examine the commonly used herbicide glyphosate and its main metabolite AMPA and looked at the off-site risk related to runoff and erosion processes in a short-term simulation experiment (Chapter 3). In order to quantify off-site transport of glyphosate by runoff and erosion, we looked at the amount of glyphosate and AMPA in the flume soil at the end of the experiment (1 h). We found that the amount of these compounds differed significantly within the soil layers ($p<0.05$) and approximately 77% of the applied glyphosate (including AMPA) remained in the 0-10 cm soil layer (Figure 6.2). Our results showed that most of the added glyphosate was concentrated in the topsoil which is in accordance with other studies (Bergström et al., 2011; Lupi et al., 2015; Rampazzo et al., 2013).

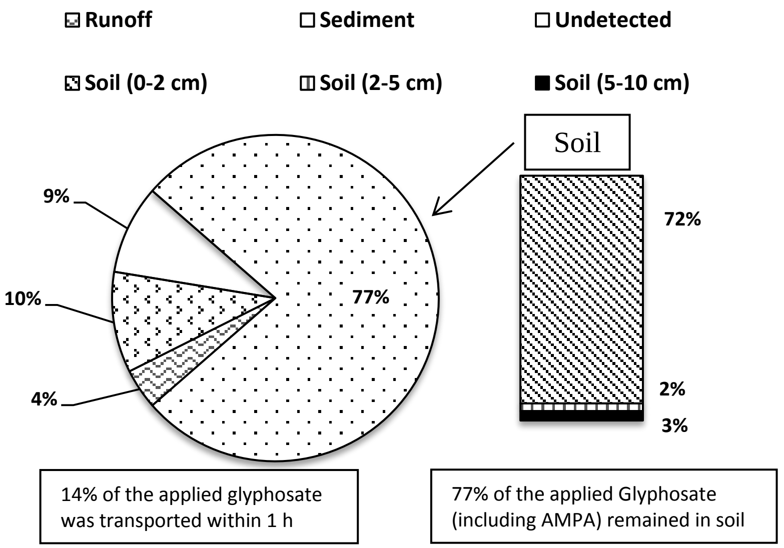

Figure 6.3 *Distribution of glyphosate (including AMPA) in soil, runoff and sediment after 1h of rainfall (% of initially applied glyphosate).*

The transport rate of glyphosate was 14% of the applied amount: 4% by runoff and 10% by sediment. This implies that the main transport mode for glyphosate and AMPA is particle-facilitated transport which is similar to the results of Degenhardt et al. (2012). About 70% of the transport of transported glyphosate (including AMPA) was observed in the first 30 min of simulated rainfall which suggests that there is a high risk of glyphosate runoff when heavy rain occurs shortly after glyphosate application. The concentrations of glyphosate and AMPA in runoff and sediment decreased with the duration of rainfall, following the power and exponent curve between rainfall duration and the concentration of glyphosate and AMPA (p<0.01) in runoff and suspended load, respectively. Although precipitation dilutes the concentration of pollutants, the level of glyphosate and AMPA in the runoff of this study was still high (>100 µg L^{-1}) after 1 h of rainfall compared to the EU limit value (0.1 µg L^{-1}) in groundwater. This high concentration of glyphosate poses a threat to the surface water quality in regions with high rainfall (Muangphra et al., 2014; Yadav et al., 2013; Zhou et al., 2013).

Pesticide in topsoil has a high potential risk of being transported off-site with soil erosion and runoff (Todorovic et al., 2014). With a thin layer of eroded soil, sediment-bound pesticides have a high risk of being transported downstream (Zhang et al., 2011b). Previous studies reported that glyphosate percolates via soil macropores to deeper soil layers (Jarvis, 2007; Lowry et al., 2004; Styczen et al., 2011a; Todorovic et al., 2014) and even to the groundwater during the rainfall (Al-Rajab et al., 2008; Kjaer et al., 2005; Magga et al., 2008; Norgaard et al., 2014; Stone and Wilson, 2006; Ulén et al., 2012). In chapter 3, we didn't find any leachate within the first 60 min of the simulation experiment. Although 5% of the added glyphosate was detected in 2-10 cm of the soil layer, the leaching risk of glyphosate under these short-term conditions is low. To the contrary, the AMPA concentration in deep soil layers was higher than the glyphosate concentration suggesting that the risks of AMPA need to be taken into account, especially in unstructured soil (Styczen et al., 2011a). In addition, we found that 9% of the applied glyphosate was undetectable in our experiment (Figure 6.2). This could be explained by glyphosate leaching into deeper soil layers or decaying to other metabolites which we didn't detect. Although the amount of glyphosate and AMPA are limited in deeper soil, studies on leaching and contamination risks for groundwater need to be conducted.

Consequently, the findings presented in Chapter 3 showed that particle-facilitated transport of glyphosate and AMPA has a high potential off-site risk, especially in highly erosive regions such as the Loess Plateau in China. Models to assess the potential risk of chemicals transported by particle-facilitated mode need to be considered (Schulz, 2004; Zhang et al., 2011b).

6.1.3 On-site fate of glyphosate and AMPA in Chinese loess soil

In Chapter 4, the characteristics of glyphosate and AMPA decay and their transport related to runoff and eroded soil particles were examined under field conditions. Our data showed that glyphosate residues are concentrated in the upper 2 cm soil layer and decay rapidly with a 3.5 d half-life following the first-order of decay in Chinese loess soil during the summer time (Figure 6.3). However, the decay can be significantly slower during the rest of the year due to long periods of low temperatures.

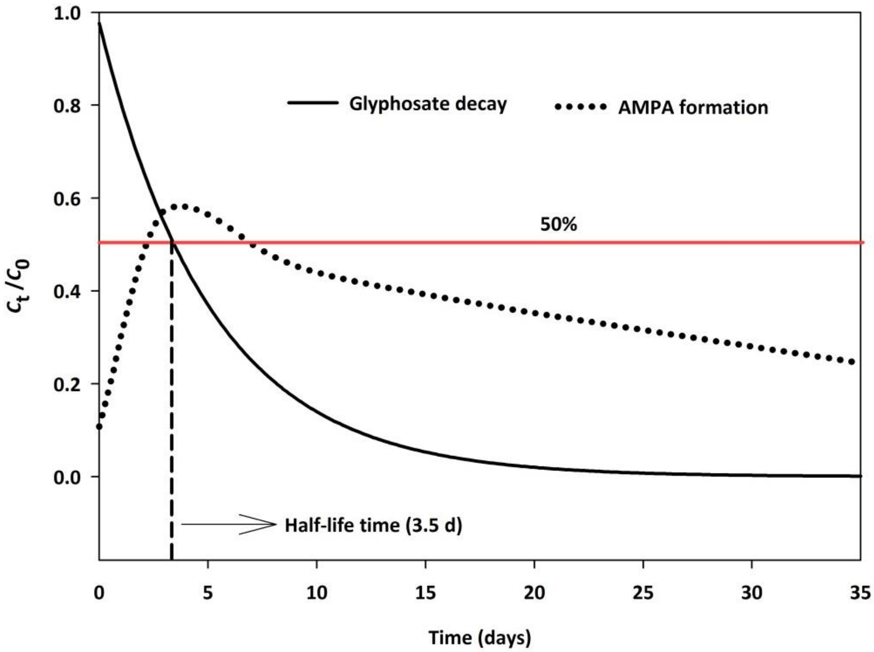

Figure 6.4 *Glyphosate decay and AMPA formation/decay and half-life time (detected glyphosate (C_t) /initial applied glyphosate (C_0)) during summer time. AMPA formation was calculated by its parent glyphosate based on molecular mass.*

Biodegradation plays an important role in glyphosate decay in soil. The half-life of glyphosate varies from 1.2 to 197.3 d (Giesy et al., 2000b). The level of pesticide residues in soil depends on individual pesticide properties as well as on their interactions with soil microbial communities (Zabaloy et al., 2012). Precipitation and temperature also influence glyphosate decay (Schroll et al., 2006; Sorensen et al., 2006). Studies have shown that glyphosate decays easily when exposed to higher temperatures, which led to obvious changes in the DT_{50} of glyphosate (Al-Rajab et al., 2008; Litz et al., 2011). In our study, the properties of glyphosate decay during the two years of monitoring were similar, indicating that glyphosate decay in Chinese loess soil is relatively stable during the summer months with high temperatures and optimal soil moisture.

The metabolite AMPA in the 0-2 cm soil layer peaked at 3 d after glyphosate was added to the soil and then declined gradually. The half-life for AMPA was estimated to be 23 d in 2012 and 35 d in 2013.. According to other studies, the half-life of AMPA ranged from 9 to 240 d (Al-Rajab et al., 2008; Al-Rajab and Schiavon, 2010; Bergström et al., 2011; Giesy et al., 2000b; Mamy et al., 2005). The behaviour of glyphosate and AMPA varies significantly in soil. AMPA is more persistent than its parent glyphosate under the same conditions (Bergström et al., 2011; Giesy et al., 2000b; Yang et al., 2015a) and thus poses a stronger risk of accumulation in the soil.

In addition, we found that the residues of glyphosate and AMPA significantly declined with soil depth which is in accordance with other studies (Lupi et al., 2015; Rampazzo et al., 2013). In deeper soil (2-10 cm), the measurement of glyphosate was near the detection limit while the AMPA concentration was higher. With a brief and low-intensity erosive rainfall, the total transported glyphosate (including AMPA) ranged from 0.31 to 0.46% of the initially applied glyphosate with around 71% of transported glyphosate accumulating in the suspended load. Thus, more attention should be paid to glyphosate transported with soil particles downstream, especially in high erosion areas.

6.1.4 Off-site risk assessment for particle-facilitated transport of pesticide related to erosion

In Chapter 5, we developed an integrated model to predict a pesticide's off-site transport due to runoff and erosion (Figure 6.5). The model is based on broadly accepted assumptions such as the convection-dispersion equation, lognormal distribution of transport related soil properties, sorption and degradation, and soil erosion processes. Furthermore, a sensitivity analysis was conducted indicating that the total mass of pesticide used is associated with the hydrology process, rainfall intensity, erosion and its decay properties.

Although many models have been developed to predict pesticide risk, most of them focus on pesticide transport in the dissolved phase, known as ARM (Donigian and Davis, 1978), CREAMS (Knisel, 1980), ANSWERS (Dillaha III and Beasley, 1983), PRZM_GW (Carsel et al., 1985), AGNPS (Young et al., 1986), LEACHM (Hutson et al., 1989), MACRO (Jarvis et al., 1994), PLM (Nicholls et al., 2000), RZWQM (Ahuja et al., 2000), PEARL (Leistra et al., 2001), GeoPEARL (Tiktak et al., 2002), and PeLM (Chen et al., 2004), ignoring the compounds bound to particles. Indeed, dissolved pesticides are immediately harmful to drinking water (Chau et al., 2015; Fuscoletti et al., 2015) but the residuals accumulated in the soil or sediment are considered to be a way of reducing pesticide mobility. Unfortunately, these accumulated pesticides adsorbed to particles can affect aquatic organisms and the human body (Zhu et al., 2015). With respect to transport as solute or particulate particles, the challenge for pesticide risk assessment is to develop pesticide transport models for pesticides that are both dissolved in water and adhered to particles while considering pesticide decay characteristics, especially in a region with extreme erosion and runoff. Fortunately, some studies use erosion models to predict pesticide risks, such as WEPP, but they do not take particle-facilitated transport into consideration. Therefore, this thesis can offer a theoretically integrated model to predict particle-facilitated pesticide transport and contribute to off-site risk assessment.

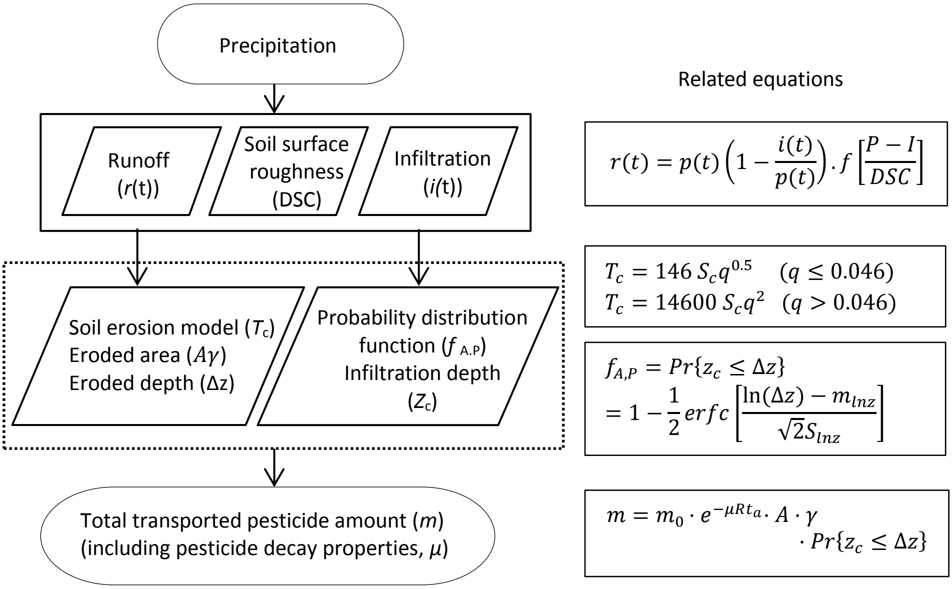

Figure 6.5 *The model structure of particle-facilitated transport of pesticides due to runoff and erosion.*

6.2 General conclusions

This thesis focused on the stakeholders' (farmers' and retailers') perspectives on the risks related to pesticide use and on the environmental fate and off-site effects of the commonly used herbicide glyphosate and its metabolite AMPA in the Wei River catchment in China. The insights gained from this research are very important for the evaluation of the exposure risks to farmers and the environment and are also valuable for understanding glyphosate and AMPA transport and decay in Chinese loess soil.

The main findings are:

- Farmers in rural China have a high level of exposure to the dangers of pesticides as a result of their lack of education and their lack of knowledge concerning the effects of pesticide exposure on both themselves and environmental systems. Older and less educated people are most at risk. Although most retailers have a comprehensive knowledge of proper pesticide use and a strong sense of responsibility towards pesticide application, their awareness of the dangers that pesticides pose to human health and the environment is still very limited. Better education programmes are urgently needed to address these problems that pose an increasing risk to farmers, consumers, and the environment.

- There is a high risk of off-site transport when erosive rainfall occurs shortly after pesticide application. More attention needs to be paid to the proper timing of pesticide application, especially in high erosion areas.
- Although glyphosate decayed rapidly, with a 3.5 d half-life in topsoil during the summertime, AMPA was more persistent than its parent glyphosate, with > 23 d half-life indicating a potential risk for spatial AMPA accumulation during the wintertime. Further study on the fate and risks of AMPA in soil needs to conducted in order to assess the risk that glyphosate poses to the environment.
- In order to assess the potential off-site risk from pesticide applications, we created an integrated model to assess off-site pesticide risk which allows us to predict the total potential mass of a transported pesticide while taking into account water infiltration, erosion, runoff, pesticide transport and degradation.

6.3 Implications

6.3.1 Implications for pesticide application and management

Pesticide pollution has become a great challenge for the sustainable development of agriculture (Rashid et al., 2010). Many studies have focused on pesticide fate, effects and treatment to reduce/eliminate pesticide risks in an environmental system (Guo et al., 2014) while only a few studies have considered pesticide safety use among farmers, agricultural workers and pesticide sellers, especially in rural areas of China (Huang et al., 2000; Huang et al., 2003; Zhang and Lu, 2007). Admittedly, understanding pesticide behaviour and finding the right methods to eliminate pesticides in the environment are really important ways to reduce pesticide pollution. However, safe pesticide use should also be emphasized (Matthews, 2008).

As the end users and distributors, farmers and retailers are directly exposed to pesticides. Their behaviour towards the safe use of pesticides plays an important role in reducing pesticide pollution, hazards, and intoxication in agricultural regions. Improper pesticide application, including incorrect selection, overuse, or spraying during harvesting, can lead to a high amount of residues that are harmful to consumers and the environment on the products. Meanwhile, the timing of pesticide application is another factor that influences the prevalence of pesticides in the environment. The application of pesticides just before an imminent rainstorm, for example. Educational programmes targeting proper application and management of pesticides should take timing, dose and frequency of pesticide application into account and emphasize the importance of avoiding pesticide application before imminent rainstorms. This programme should also inform farmers about the details concerning safe pesticide management practices, and provide a comprehensive list of practising benefits and disadvantages, including health and environmental impacts. Thus, some training programmes need to be carried out to improve farmers' ability to avoid application mistakes and potential risks to the environment.

6.3.2 Implications for pesticide regulations and supervision policies

It is widely recognized that the pressure to use pesticides in agricultural development can be detrimental to both the environment and to the productivity of farmland. However, there are a number of barriers to the design and implementation of policies which would effectively relieve these pressures and improve the supervision system. These barriers include the difficulties of accessing agronomic data and making it available to the proper authorities in order to design policy measures that would be efficient for a range of different agricultural conditions. Furthermore, the local economic development, which benefits from the pesticide market, influences policy making which results in policies that are often changed and are not supported by the local government. Global differences in pesticide regulations cause further problems in the case of international trade, especially for developing countries that still use toxic pesticides that are not authorized for use in developed nations (Handford et al., 2015).

Current Chinese pesticide legislation was changed in 2009 when China implemented a series of new regulations that restricted the registration of new pesticides and thus prevented them from getting into circulation (Liu et al., 2015b). According to the new rules, in order to register a new pesticide, a company must provide information regarding a pesticide's ingredients, production process, chemical data, safety data, labelling, user's manual, business license, and study reports. This information has to be entered into a public database that is available to authorities, institutions and companies. Although the regulations are complete, the policies concerning supervision seem to give rise to some dilemmas from a socioeconomic and sustainable development point of view. This is why some banned pesticides are still available on the market, especially in rural areas where the supervision system is insufficient. Hence, policies on pesticide supervision and environmental monitoring systems should be strengthened, not only on the national scale but also on smaller regional and local scales.

In order for such policies to be sufficiently strengthened, consideration needs to be given to ways in which the policy can be better directed to address a range of concerns about the balance of socioeconomic and environment sustainability on the local, regional, and national level. Policy measures could then be affectively aligned and better supervised to increase the use of the most effective forms of management and support in order to progress towards a predominantly results-based approach in agricultural and environment policies rather than falling back on habitual practices.

6.3.3 Implications and recommendations for the pesticide risk assessment model developed in this project

Based on the results of this thesis, especially those showing that a significant amount of pesticide can be transported by soil particles in a single short-term erosive rainfall, a theoretical model to predict off-site pesticide risk related to soil erosion has been developed to assess pesticide risk, particularly in high erosion areas like the Wei River catchment in China. Similar to other studies, this model for pesticide risk assessment refers to pesticide behaviour, transport mode and related hydrological processes in soil instead of only focusing on the pesticides dissolved in water.

Our research and our model indicate that runoff, infiltration, sorption, degradation, and erosion are the factors that play key roles in predicting the total off-site transport of pesticides related to soil erosion. Further research should focus on:

1) The accurate representation of the infiltration process which determines the depth of pesticides in soil layers. According to our assumptions, all resident soil water is pushed downwards by infiltrating water (Wierenga, 1977) thus causing the infiltration front to be at a depth equal to the cumulative amount of infiltrated water, $I(t)$, divided by θ_{fc}. In field scale monitoring, however, the resident soil water doesn't infiltrate deeper soil layers

completely. It is also affected by the water dispersion in and out of the soil entrained within runoff.

2) Examining how total soil loss is calculated. We made calculations based on the maximum amount of sediment that could be transported. With this calculation, the amount of the total eroded soil can be over-evaluated. Thus, the validation work needs to be done before calculating the eroded depth. Furthermore, other erosion models, such as LISEM, SWAT and WEPP could also be considered and integrated into the erosion part of the model to simulate eroded soil. Drawing on and integrating different models related to pesticide transport through erosion would enable the mapping of the pesticide risks on different scales.

6.4 Research challenge and future studies

Since we interviewed farmers and retailers, this thesis contributes to a greater insight and understanding of pesticide risk potential to both the environment and human health. It is an approach that aims to reduce or eliminate pesticide risks at their source. Some challenges were encountered during the course of this thesis research which included communicating with local people, collecting reliable data and understanding people's experience with pesticide use. However, the long-term study of glyphosate fate under field conditions is yet another challenge, especially when considering multiple erosive rainfalls. Pesticide application also affects soil quality and the soil ecosystem. We need more studies examining the effects of pesticides on soil microbial activities In addition, the developed model in this thesis is an integrated pesticide transport model which needs more validation and calibration in different scenarios and soils.

Based on the findings of this thesis regarding glyphosate and AMPA transport related to soil erosion and decay, it is worthwhile to continue this research on pesticide risk assessment in China. Although ambitious, several studies related to this research could be conducted such as:

- Upscaling the survey to include more stakeholders.
- Using multiple applications and erosion events to assess off-site pesticide risks.
- Examining the roles of measurements in reducing pesticide risks off-site.
- Looking at the effects of glyphosate and AMPA residues on soil quality.
- Field scale monitoring and model validation.

Finally, we contributed to a better understanding of people, processes, pesticide chemistry and soil dynamics that will give insight into how to minimize pesticide use and related on-site/off-site risks for the benefit and wellbeing of the farmers, the consumers and the environment.

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English summary

With increasing population and food demand, crop productivity and food safety have become a great challenge worldwide. In order to reduce or eliminate yield losses and maintain high product quality in agricultural system, pesticides have been used intensively and this trend is undoubtedly increasing in the next decades. Indeed, pesticide boosts productivity and domestic economy but with the intensive use, unfortunately, the residuals of pesticide are frequently detected in water, soil and even in food products.

According to the China Annual Statistics, China has become the largest country to produce, export and use pesticides in the world. Tons of pesticides are input in farmland leading to problems such as environmental pollution affecting human health. With the limited size of cultivation land and the urgent food demand, the annual rate of pesticide application in China is increasing, especially in some hotspots. Due to the insufficient supervision and legal frameworks, some highly toxic, persistent, and bioaccumulative pesticides are still commercially available. The pesticide exposure risks for farmers resulting from the improper application methods are ignored as well as the lack knowledge and awareness of farmers on risks associated with pesticide use. In addition, the behaviour of pesticides in environmental system varies significantly with the different properties of pesticide and conditions, such as weather, rainfall, soils and land use. Therefore, the risk assessment for pesticide use needs to take these factors into account.

Chapter 2 presented results on the information for the knowledge and awareness of pesticide risks via face-to-face interview among farmers (209) and retailers (20) in two rural regions (Qianyang County (S1) and Chencang County (S2)) of the Wei River catchment in China where the modes of farming and the state of erosion are very different. The results showed that farmers learned about the use and risk related to of pesticide use mainly by oral communication (p<0.01), rather than by introduction labelled on pesticide package bag/bottle and media tools (TV/newspaper/Internet/books). Protective measures were inadequate and washing hands (>70%) was the most common mode of personal hygiene after spraying, comparing to wearing masks, showering, and changing clothes. Regarding to dealing with the packages or containers of pesticide, farmers dumped them directly onto the land or into water and over 85% of farmers

claimed to use illegal pesticides. Compared to farmers, pesticide retailers were well-informed and highly conscious of their responsibility for the safe use of pesticides. A canonical correspondence analysis indicated that educational level and age differed strongly between the two regions and contributed greatly to the risks resulting from pesticide use ($p<0.01$). The study recommends that educational programmes targeted to age groups, proper disposal of pesticide waste, and sufficient supervision from authorities should be considered for improving the levels of knowledge and awareness of the farmers with respect to pesticide risk for human health and the environment. The supervisory mechanism and environmental monitoring systems for pesticides should be strengthened and the nation scale survey on safety use of pesticide and its risk on environment and human health should also be evaluated. The large agricultural population in China suggests that all stakeholders, including governmental agencies, producers, retailers, and farmers, should unite to address the risks from the use of pesticides for farmers and the environment and develop sustainable production systems.

Chapter 3 assessed the short-term transport (1 h duration, 1 mm min^{-1} rainfall) of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) related to erosion and runoff on bare loess soil with different slopes (10° and 20°)and application rates (3.6 kg ha^{-1} and 7.2 kg ha^{-1}) in hydraulic flumes. Significant power and exponent function described a significantly negative relation between rainfall duration and the content of glyphosate and AMPA ($p<0.01$) in runoff and suspended load, respectively. Glyphosate and AMPA content in the runoff and sediment depended more on the initial rate of application than on the slope gradients. The transport rate of glyphosate (including AMPA) by runoff and suspended load was approximately 4% and 10% of the applied amount, respectively indicating that it mainly underlies particulate transport. The glyphosate and AMPA content in the flume soil at the end of the experiment (after 1 h) decreased 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. Thus, the risk of leaching was low. In view of loss of 14 % of the initially applied Glyphosate after 1 h, “buffer zone”, referred as the protection area for ecosystem discharge between farming land and public rivers, is strongly recommended, especially in regions where rain-induced soil erosion is common.

In chapter 4 glyphosate decay, erosion and runoff related transport of glyphosate and AMPA were assessed at different slopes (10° and 20°) and application rates (3.6 kg ha^{-1} and 7.2 kg ha^{-1}) under field condition during 35 d, September-October in 2012 (16.8±2.1°C with 35 mm rainfall in total) and July-August in 2013 (27 ± 2.3°C with 74 mm rainfall in total). The results showed that glyphosate decayed rapidly resulting in a half life time of 4 d following the first-order of decay. AMPA correspondingly, peaked at 3 d after glyphosate added and then declined gradually, with >23 d of half-life time in loess soil. The residues of glyphosate and AMPA significant declined with soil depth ($p<0.05$) independently of the slope inclinations and application rates. Glyphosate leaching was low, approximately 2% of the initial applied glyphosate, due to the limit of glyphosate detected in deeper soil (2-10 cm) while AMPA was detected in 2-10 cm soils. Only one erosive rainfall occurred in the experimental period, leading to low runoff and erosion rates. The total rates of glyphosate transport were similar at the different slopes and application rates, ranging from 0.31 to 0.46% of the applied glyphosate, and 29 and 71% of the transported glyphosate accumulates in runoff and suspended load, respectively. This implies that intense rains are an essential factor for the off-site transport of glyphosate and AMPA and can be a strong risk in regions with high soil runoff and erosion rates. Furthermore, particulate-facilitated transport of glyphosate should receive more attention in the regions where soil erosion frequently occurs. Interestingly, the content of glyphosate and AMPA in suspended load was much higher than that detected in plot 0-2 cm soil. This suggested that even though the transported glyphosate is limited, the off-site risk of glyphosate and AMPA is high. Consequently, a realistic erosion-pesticide model should be developed that can simulate the particulate-facilitated transport of glyphosate and its off-site risks involving decay processes.

Chapter 5 developed a parsimonious integrative model for pesticide transport by runoff and erosion which explicitly accounts for water infiltration, erosion and runoff, and pesticide transport and decay process in soil. The conceptual framework is based on broadly accepted assumptions such as the convection-dispersion equation, lognormal distribution of transport related soil properties, sorption and decay, and erosion. However, to illustrate the concept, assumptions are made with regard to runoff in relatively flat agricultural fields (<5°), by ignoring dispersion and to enable erosion to be modelled by a functional relationship. A sensitivity analysis showed that the total mass of pesticide associated with soil eroded by water scouring with the increasing of slope, rainfall intensity and soil field capacity. As the micro-topography of the soil surface becomes more distinct, the mass of transported pesticide decreases. The decay rate and spraying time of pesticide before erosion affects the total of transported pesticide. The mechanisms involved in pesticide displacement, such as runoff, infiltration, soil erosion, and pesticide transport and decay in the topsoil, were all explicitly accounted for, so the mathematical complexity of their description can be high, depending on the situation.

Overall, the outcome of this study indicates that it is urgent to improve farmers knowledge and awareness on pesticide use in order to reduce pesticide risks before pesticide applied in environmental system. The rapid decay of glyphosate to AMPA in loess soil suggests that on-site risks of glyphosate is mainly related to AMPA, especially under warmer climatic conditions. The off-site transport of glyphosate in our study was about 14% of the applied dose after 1 h of rainfall indicating that the off-site risks of glyphosate should be taken into account in regions highly prone to soil erosion. The concept of particulate transport elaborated in chapter 5 should be incorporated in existing erosion models such as LISEM to predict off-site effects of glyphosate applications.

Nederlandse samenvatting

Met een toenemende bevolking en vraag naar voedsel, zijn gewasproductie en voedselveiligheid wereldwijd een grote uitdaging. In de landbouw worden pesticiden toegepast ter voorkoming of vermindering van ziektes en plagen die leiden tot een kwantitatieve vermindering van de opbrengst. Ook worden ze gebruikt om de kwaliteit van de productie te onderhouden. De afgelopen jaren is het gebruik sterk toegenomen. Ongetwijfeld zal deze trend zich de komende decaden voortzetten. Alhoewel pesticiden de productiviteit wel degelijk fors kunnen verhogen en hiermee de plaatselijke economie stimuleren, worden door het intensieve gebruik ervan helaas ook vaak residuen van pesticiden aangetroffen in het water, de bodem en zelfs in voedselproducten.

Volgens de Chinese jaarstatistieken is China wereldwijd uitgegroeid tot de grootste producent, exporteur en gebruiker van bestrijdingsmiddelen. Grote hoeveelheden bestrijdingsmiddelen worden toegepast op landbouwgrond, hetgeen leidt tot problemen zoals milieuvervuiling, wat weer schadelijk kan zijn voor de gezondheid van mensen. Door de beperkte hoeveelheid cultuurgrond en de dringende vraag naar voedsel neemt het gebruik van pesticiden in China jaarlijks toe, vooral in bepaalde gebieden. Door gebrek aan voldoende toezicht en wetgeving zijn er nog steeds een aantal zeer giftige, persistente en bio-accumulerende pesticiden in de handel verkrijgbaar. Doordat deze bestrijdingsmiddelen onjuist worden toegepast en door het gebrek aan kennis en besef over de gevaren, lopen landbouwers risico’s als zij aan deze stoffen worden blootgesteld. Het gedrag van pesticiden in het milieu varieert sterk van soort tot soort. Hierbij zijn ook het weer (temperatuur en neerslag), de bodem en het landgebruik van essentieel belang. Daarom moet met al deze factoren moet rekening worden gehouden bij de risico beoordeling van een pesticide.

In hoofdstuk 2 van dit proefschrift worden de uitkomsten besproken van persoonlijke interviews die gehouden zijn onder landbouwers (209) en detailhandelaars (20) over de kennis en het besef van de risico’s van pesticiden in twee landelijke gebieden in het stroomgebied van de Wei rivier in China: Qianyang County (S1) en Chencang County (S2). De vormen van landbouw en erosie zijn hier heel verschillend. De resultaten tonen aan dat de boeren hun kennis over het gebruik van pesticiden en de aan het gebruik hiervan verbonden risico's voornamelijk verkregen door mondelinge communicatie (*p* <0.01). Er werd nauwelijks kennis vergaard door de informatie op de verpakking van pesticiden te lezen of via de media (TV / krant / Internet / boeken). Beschermende maatregelen waren ontoereikend en na toediening van de pesticide was het wassen van de handen (> 70%) de meest voorkomende vorm van persoonlijke hygiëne. Andere maatregelen zoals het dragen van maskers, douchen en omkleden kwamen veel minder voor. De verpakkingen van pesticiden werden meestal gedumpt op de bodem of in het water en meer dan 85% van de boeren beweerde illegale bestrijdingsmiddelen te gebruiken. De detailhandelaren waren wel goed geïnformeerd en waren zich zeer bewust van hun verantwoordelijkheid voor het veilig gebruik van pesticiden. Een canonische correspondentieanalyse gaf aan dat er een groot verschil was in opleidingsniveau en leeftijd tussen de twee regio's en dat dit in belangrijke mate bijdroeg aan de kennis over het gebruik van pesticiden (*p* <0.01). Om het kennisniveau en het bewustzijn van de boeren met betrekking tot gezondheidsrisico’s en milieu te verbeteren beveelt deze studie educatieve programma’s aan, gericht op verschillende leeftijdsgroepen en het op de juiste manier omgaan met afval, waarbij voldoende overheidstoezicht moet worden overwogen om het bewustzijns- en kennisniveau van boeren aangaande het gebruik van pesticiden en hun invloed op het milieu en de menselijke gezondheid te verbeteren. Het controle- en monitorsysteem voor het milieu aangaande bestrijdingsmiddelen moet worden uitgebreid. Ook moet de enquête over veilig gebruik van pesticiden en de risico’s ervan voor milieu en menselijke gezondheid op nationale schaal worden uitgevoerd en geëvalueerd. De grootte van de agrarische bevolkingsgroep in China geeft aan dat alle belanghebbenden, met inbegrip van overheidsinstanties, fabrikanten, handelaars en boeren zich zouden moeten verenigen om de risico's van het gebruik van pesticiden voor de boer en het milieu aan te pakken en zo een duurzame productiemethode te ontwikkelen.

In hoofdstuk 3 wordt het korte-termijn transport (1 h, 1 mm min^{-1}) van glyfosaat en zijn metaboliet aminomethylfosfonzuur (AMPA) onderzocht in relatie tot erosie en afstroming op kale lössgronden met verschillende hellingen (10° en 20°) en toedieningshoeveelheden (3.6 kg ha^{-1} en 7.2 kg ha^{-1}). Het onderzoek is uitgevoerd met behulp van hydraulische goten. Machts- en exponentiele functies laten een significant negatief verband zien tussen de neerslagduur en de hoeveelheid glyfosaat en AMPA (p<0.01) in respectievelijk oppervlakkige afvoer en sediment. Het glyfosaat en AMPA-gehalte in zowel afvoer als sediment hangt meer af van de opgebrachte hoeveelheid dan van de helling. De getransporteerde hoeveelheid glyfosaat (inclusief AMPA) via afvoer en sediment is respectievelijk zo’n 4% en 10% van de gegeven hoeveelheid. Dit geeft aan dat vooral het sediment transport hieraan bijdraagt. Het glyfosaat en het AMPA-gehalte in de gootbodem aan het eind van het experiment (na 1 uur) neemt significant af met de diepte (p<0.05) en bedraagt ongeveer 72, 2, en 3% van de toegediende hoeveelheid glyfosaat (inclusief AMPA) in de respectievelijke bodemlagen van 0-2, 2-5 en 5-10 cm diepte. Derhalve is het risico op uitspoeling laag. Vanwege het verlies van 14% glyfosaat na 1 uur wordt het gebruik van een bufferzone sterk aanbevolen. Deze functioneert dan als beschermingsgebied voor afvoer uit het ecosysteem tussen landbouwgrond en open waterlopen vooral in regio's waar bodemerosie ten gevolge van neerslag voorkomt.

In hoofdstuk 4 worden de afbraak van glyfosaat en de hoeveelheid erosie en oppervlakkige afvoer met het hieraan gerelateerde transport van glyfosaat en AMPA onderzocht. Hierbij zijn verschillende hellingen (10° en 20°) gebruikt en verschillende hoeveelheden (3.6 kg ha^{-1} en 7.2 kg ha^{-1}) toegediend. Gedurende 35 dagen werden de processen gevolgd en wel in de periodes September-Oktober 2012 (16.8±2.1°C met 35 mm neerslag) en Juli-Augustus 2013 (27 ± 2.3°C ; 74 mm neerslag). De resultaten tonen aan dat glyfosaat snel afbreekt, resulterend in een halfwaardetijd van 4 d volgens een eerste-orde afbraaksysteem. Navenant piekte het AMPA gehalte 3 d na de glyfosaat toediening en daalde vervolgens geleidelijk met een halfwaardetijd die groter is dan 23 d in de beschouwde lössgrond. De hoeveelheid residuen van glyfosaat en AMPA daalt significant met de bodemdiepte (p<0.05), onafhankelijk van de bodemhelling en de toegediende hoeveelheden. Doordat de gedetecteerde hoeveelheid van glyfosaat in de diepere bodemlagen (2-10 cm) gering was, was de uitspoeling gering en bedroeg slechts zo'n 2% van de toegediende hoeveelheid. AMPA werd daarentegen juist waargenomen in de 2-10 cm bodemlaag. Er is slechts één erosie veroorzakende regenbui opgetreden gedurende de experimentele periode. Dit leidde tot een lage afvoer en geringe erosie. De totale hoeveelheid glyfosaat transport was vergelijkbaar bij de verschillende hellingen en toedieningshoeveelheden. Dit varieerde van 0.31-0.46% van de toegediende hoeveelheid. Hiervan cumuleerde 29% in afvoerwater en 71% in sediment. Dit houdt in dat regenbuien met een hoge neerslagintensiteit een essentiële factor vormen voor transport van glyfosaat en AMPA naar de omgeving en dat dit derhalve een groot risico kan zijn in regio's met hoge oppervlakkige afvoeren en erosie-snelheden. Bovendien moet het transport van glyfosaat met het sediment meer aandacht krijgen in regio's waar bodemerosie vaak voorkomt. Interessant is dat de hoeveelheid glyfosaat en AMPA in sediment veel hoger was (respectievelijk 35-72 µg g^{-1} en 10-21 µg g^{-1}) dan waargenomen in de plot op 0-2 cm diepte (12-26 µg g^{-1} en 8-12 µg g^{-1}). Dit suggereert dat, ofschoon de getransporteerde hoeveelheid glyfosaat beperkt is, het risico van glyfosaat en AMPA voor de omgeving hoog is. Bijgevolg moet er een realistisch erosie- en bestrijdingsmiddelenmodel worden ontwikkeld waarmee sediment transport van glyfosaat inclusief afbraak en de omgevingsrisico’s hiervan kunnen worden gesimuleerd.

In hoofdstuk 5 wordt een eenvoudig geïntegreerd model ontwikkeld voor het transport van pesticiden door oppervlakkige afvoer en erosie. Dit model houdt expliciet rekening met processen zoals infiltratie van water, erosie, oppervlakkige afvoer, het transport van pesticiden en de afbraak hiervan in de bodem. Het conceptuele kader is gebaseerd op reeds breed geaccepteerde uitgangspunten voor de convectie-dispersie vergelijking en lognormale verdelingen van bodem-gerelateerde transportprocessen, sorptie, afbraak en erosie. Echter, om het concept te illustreren, worden aannames gedaan met betrekking tot afvoer in relatief vlakke landbouwgebieden (<5°). Er wordt voorbijgegaan aan dispersie en erosie wordt gemodelleerd door een functionele relatie. Een gevoeligheidsanalyse laat zien dat bij watererosie de totale massa van bestrijdingsmiddelen gerelateerd is aan een toenemende helling, neerslagintensiteit en veldcapaciteit van de bodem. Als het micro-reliëf van het bodemoppervlak duidelijker wordt, neemt de hoeveelheid getransporteerde pesticide af. Zowel de afbraaksnelheid als de tijd die verstreken is sinds de laatste pesticide-toediening vóórdat een erosie gebeurtenis plaatsvindt is van invloed op de totale hoeveelheid vervoerde pesticide. Er is expliciet rekening gehouden met transportprocessen zoals oppervlakkige afvoer, infiltratie, bodemerosie en pesticide-transport en afbraak in de bovengrond, hetgeen, afhankelijk van de situatie, de wiskundige complexiteit groot kan laten worden.

Samenvattend laat de uitkomst van deze studie zien dat er een dringende noodzaak is om de kennis en het besef van landbouwers in China aangaande het gebruik en gevaar van pesticiden te vergroten alvorens deze worden toegediend waardoor de risico’s voor het milieu verminderd kunnen worden. De snelle afbraak van glyfosaat in lössgronden suggereert dat voor deze pesticide de milieurisico’s klein zijn, vooral onder warmere weersomstandigheden. De hoeveelheid getransporteerde glyfosaat naar de omgeving was in deze studie ongeveer 14% h^{-1}, hetgeen aangeeft dat het risico van glyfosaat in erosiegevoelige gebieden aanmerkelijk is. Het concept van sediment transport, uitgewerkt in hoofdstuk 5, kan in de bestaande erosie modellen zoals LISEM worden toegepast om zo de effecten van glyfosaat toedieningen voor de omgeving te kunnen voorspellen.

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Curriculum Vitae

Xiaomei Yang was born on 22 December, 1983 in China. She obtained her BSc degree in Environment Science in Shaanxi Normal University in July 2007. In the same year, she entered Graduate University of Chinese Academy of Sciences, Beijing. After one year studying in Beijing, she did her master thesis in Institute of Soil and Water Conservation (ISWC), Chinese Academy of Sciences and Ministry of Water Resources. She obtained a Master of Science (MSc) Degree in Ecology in July 2010. After completing the MSc programme, Xiaomei worked as an assistant of Prof. Jimin Chen in ISWC including project and laboratory management. Meanwhile, she was invited as secretory to organize "The First Plenary Meeting of World Association of Soil and Water Conservation and the International Conference on Combating Land Degradation in Agricultural Areas (LANDCON 1010)" held in 11-15th October, 2010. In January 2011, Xiaomei joined the Land Degradation and Development Group (currently named as Soil Physics and Land Management) of Wageningen University to start her PhD study. Her PhD project was funded by China-Netherlands Joint Scientific Thematic Research Programme (JTSP) supported by the External Cooperation Program of the Chinese Academy of Sciences and Netherlands Organization for Scientific Research. During her PhD study, she supervised a master student and presented her research results at both international and national conferences.

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1. **Yang, X.**, Van Der Zee S.E.A.T.M., Gai, L., Wesseling J.G., Ritsema, C.J., Geissen, V., 2016. Integration of transport concepts for risk assessment of pesticide erosion. Science of The Total Environment 551-552: 563-570.
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1. **Yang, X.**, Wang, F., Célia B., Van Dam, R., Mol H., Geissen, V., Ritsema, C.J. Decay characteristics of glyphosate in Chinese loess soil: plots observation. SENSE-WIMEK Symposium: Hazard, Risk and Sustainability in the Soil Environment, 14 October, 2015, Wageningen, the Netherlands. (Poster)
2. **Yang, X.**, Geissen, V., Ritsema, C.J. Development of strategies to improve hydrological and environmental conditions in Wei River catchment, China. Joint Scientific Thematic Research Programme (JSTP): Water management in relation to climate change and sea level rise, 7-9 September, 2015, Peking University, Beijing, China. (Oral presentation)
3. **Yang, X.**, Wang, F., Célia B., Meng L., Van Dam, R., Mol H., Geissen, V., Ritsema, C.J. Glyphosate decay and transport related with soil erosion in loess soil, china, Wageningen Soil Conference, 23-27 August, 2015, Wageningen, the Netherlands. (Poster)
4. **Yang, X.**, Wang, F., Célia B., Ritsema, C.J., Geissen, V. How runoff and particulate transport processes influence the fate of glyphosate and AMPA in soils? 20th World Congress of Soil Science, 8-13 June 2014, Jeju Korea. (Poster)
5. **Yang X.** Critical thinking in scientific research. Symposium on Soil and Water Conservation, 27 September, 2013, Yangling, China. (Oral presentation)
6. **Yang X.**, Wang F., Meng L., Ritsema C.J., Geissen V. Farmers and retailers' knowledge, awareness of the risk of pesticides: a case study in Wei River catchment, China. The 2nd WASWAC World Conference: the threats to land and water resources in the 21st century: prevention, mitigation and restoration, 4-10 September 2013, Chai Ran, Thailand. (Oral presentation)
7. **Yang X.**, Wang Z. Erosion processes on loess hillslope: rill and interrill erosion. Symposium on Soil and Water Conservation, 18 October, 2012, Yangling, China. (Oral presentation)
8. **Yang X.**, Wang Z., Liu J., Yuan Y. Rill and interrill erosion processes on loess hillslope. IAHS-ICCE International Symposium on Erosion and Sediment Yields in the Changing Environment, 11-15 October, 2012, Chengdu, China. (Oral presentation)

SENSE

Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment

DIPLOMA

For specialised PhD training

The Netherlands Research School for the
Socio-Economic and Natural Sciences of the Environment
(SENSE) declares that

Xiaomei Yang

born on 22 December 1983 in Shaanxi, China

has successfully fulfilled all requirements of the
Educational Programme of SENSE.

Wageningen, 9 May 2016

the Chairman of the SENSE board	the SENSE Director of Education
Prof. dr. Huub Rijnaarts	Dr. Ad van Dommelen

The SENSE Research School has been accredited by the Royal Netherlands Academy of Arts and Sciences (KNAW)

KONINKLIJKE NEDERLANDSE
AKADEMIE VAN WETENSCHAPPEN

The SENSE Research School declares that **Ms Xiaomei Yang** has successfully fulfilled all requirements of the Educational PhD Programme of SENSE with a work load of 53.3 EC, including the following activities:

SENSE PhD Courses

- Research in Context Activity: 'Chair of organising committee for two symposiums on Water and Soil Conservation in China' (2012 and 2013)
- Environmental Research in Context (2013)
- Introduction to R for Statistical Analysis (2014)
- Linear Model (2014)
- Human Induced Soil Degradation (2014)

Other PhD and Advanced MSc Courses

- Humanities and Technology Revolution, University of Chinese Academy of Sciences (2012)
- Advanced English, University of Chinese Academy of Sciences (2012)
- Principle and Technology of Soil Erosion Predication, University of Chinese Academy of Sciences (2012)
- Technology of Soil Conservation and Desert Combating, University of Chinese Academy of Sciences (2012)
- LISEM modelling practical, Wageningen University (2014)
- Information Literacy including EndNote Introduction, Wageningen University (2014)

External training at a foreign research institute

- Rainfall simulator training, Institute of Soil and Water Conservation, Chinese Academy of Sciences and Water Ministry Resources, China (2012)
- Training in LC-MS/MS methodology, RIKILT and Wageningen University (2013)

Management and Didactic Skills Training

- Teaching in the MSc course 'Trade-off on Agricultural Development and Environmental Security', Wageningen University (2014)

Oral Presentations

- *Rill and interrill erosion processes on loess hillslope.* IAHS-ICCE International Symposium on Erosion and Sediment Yields in the Changing Environment, 11-15 October 2012, Chengdu, China
- *Erosion processes on loess hillslope: rill and interrill erosion.* International Youth Forum on Soil and Water Conservation (IYFSWC), 18 October 2012, Yangling, China
- *Farmers and retailers' knowledge, awareness of the risk of pesticides: a case study in Wei River catchment, China.* The 2nd WASWAC World conference: The threats to land and water resources in the 21th century, 4-10 September 2013, Chai Ran, Thailand
- *Critical thinking in scientific research.* International Youth Forum on Soil and Water Conservation (IYFSWC), 27 September 2013, Yangling, China

SENSE Coordinator PhD Education

Dr. ing. Monique Gulickx