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Weather dependent dynamics of the herbicides florasulam, carfentrazone-ethyl, fluroxypyr-meptyl and fluroxypyr in wheat fields through field studies and computational simulation

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HIGHLIGHTS

- Modelling simulation was verified by field trials.
- Fates of pesticides were clarified by field trials and modelling.
- Temperature difference of 3 °C resulted in lower than 15% half-life difference.
- Higher precipitation leaded to faster pesticide degradation.

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ABSTRACT

A dynamic model of dynamiCROP was applied to study environmental fate and behavior of four herbicides in wheat including florasulam, carfentrazone-ethyl, fluroxypyr-meptyl, and fluroxypyr. Meantime, their residue in wheat and dissipation half-lives in plant determined by field trials using QuEChERS liquid chromatography tandem mass spectrometry were used to verify modelling results. The combination of experimental verification and modelling prediction deciphered the fate of four pesticides in wheat field ecosystem. Besides, temperature difference of 3 °C only resulted in lower than 15% half-life difference. By quantifying the contribution of temperature, the predominant role of rain on pesticide dissipation was highlighted for the first time, namely higher precipitation leaded to faster degradation and *vice versa*.

1. Introduction

Nowadays, pesticides are widely used to increase cropping intensity and yield by controlling weeds, insects, fungi, and other unwanted pests which potentially damage crop yield as well as quality (Fantke et al., 2011a). However, pesticides may also reach nontarget areas and species *via* wind drift, surface runoff, leaching, and by-stander exposure. More importantly, pesticide residues in crop may lead to risks for humans *via* consumption. As they are inherently toxic to living organisms, pesticides are likely to affect human health, pollute natural resources, and disturb the equilibrium of the ecosystem. Thus, not only pesticide misuse against good agricultural practice but also the perception of the general public of minimizing pesticide residue and environmental concentrations have been global environmental protection and food safety issues, due to the crucial role of consumer perception and farmer behavior in pesticide application (Koleva et al., 2011; Fantke et al., 2012a).

The dissipation information of pesticides in plants may provide better understanding of the complex behavior of pesticides in the ecosystem finally leading to residues that humans are exposed to

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(Jacobsen et al., 2015; Fantke et al., 2013). Those behaviors include not only volatilization, washoff, leaching, hydrolysis, chemical and biological degradation, and other individual processes reducing the amounts in plants after application (Fantke and Juraske, 2013), but also important behaviors which increase amounts in plants, such as root uptake from soil (Koleva et al., 2011). Besides, those half-lives obtained from experimental data suffer from laborious field experiments and long time of plant growth.

Pesticide residue analysis requires the screening of pesticide using confirmatory techniques, among which liquid chromatography mass spectrometry (LC-MS) especially with quick, easy, cheap, effective, rugged, and safe (QuEChERS) pretreatment can meet the challenge of relatively polar pesticides with poor recoveries and false positive problems (Bruzzoniti et al., 2014). The methods have been applied, modified, and used to validate a diverse range of target compounds and matrices, especially in food matrices (Bruzzoniti et al., 2014) including vegetables, fruits, and many other matrices (Anastassiades et al., 2003; Lehotay et al., 2010; Parejaa et al., 2011; Stahnke et al., 2009; Wilkowska and Biziuk, 2011; Wong et al., 2010). Despite of time, labor, and solvent volumes are dramatically reduced by adopting QuEChERS LC-MS, sample determination and field experiments are still necessary to obtain pesticide residues and half-lives. It is also challenged to elucidate the enigmatic dissipation fate of pesticides in plants. Thus, models have been developed to give deeper insights into specifics of pesticide-plant-environment systems and decipher the black box.

Fantke et al. have reviewed a wide range of crop-specific uptake models (Fantke et al., 2011a). Some of the models have been designed to focus on cereals (Fantke et al., 2011a; Rein et al., 2011), others on vegetables (Fujisawa et al., 2002; Juraske et al., 2009) or root crops (Trapp et al., 2007; Juraske et al., 2011), and yet others on fruit trees (Paraíba, 2007). Such models have been usually based on ordinary first order kinetics with constant coefficients describing substance elimination and inter-compartment transfer processes. And they have required a large set of crop and chemical specific input parameters.

To simplify this situation, dynamic models have been set up to simulate the dynamic system behavior. Mathematically, a dynamic system can be described by a set of ordinary first order linear differential equations with constant coefficients. Thus, the compartmental system and the chemicals' behavior can be equaled to solve a typical multi-compartment mass balance problem. Mass balance can be solved by either numerical method or analytical method (Rein et al., 2011; Hertwich, 2001). Yet the analytical methods are preferred because the mass balance can thus either be solved for each compartment individually or for all compartments at the same time, of which the latter provides high transparency (Fantke et al., 2013).

Furthermore, different analytical methods exist, e.g. Laplace transform or matrix decomposition. Both have been successfully applied (Fantke et al., 2011a,b; Hertwich, 2001; Ott et al., 2003; von Waldow et al., 2008). However, matrix decomposition provides more convenient and direct approach (Fantke et al., 2013).

Among reported models, dynamiCROP (http://dynamicrop.org) has unprecedentedly harmonized the problem of transparency and flexibility (Fantke et al., 2011a, 2013, 2012b) and thus distinguished itself. In dynamiCROP, the plant-environment system includes environmental compartments and plant compartments. Within and between those compartments, pesticides experience initial mass distribution, bioaccumulation and translocation *via* xylem and phloem, and transformation and translocation including diffusive and advective transfer. They are all described by first-order rate coefficients. Those differential equations are solved by matrix algebra to simulate the full dynamic system. Thus, model outputs (pesticide residues per kg applied) become a function of model variables (substance, crop, and environmental properties). It is not only that model outputs can be directly compared with measured residues. It is also that human intake and health risk can be predicted. More importantly, its results demystify the behavior of pesticides in the plant-environment system. Yet there is a lack of experimental verification up to now, with only those reported in wheat (Fantke et al., 2011a), passion fruit (Juraske et al., 2012), tomato (Fantke et al., 2011b), potato (Fantke et al., 2011b), rice (Fantke et al., 2011b), apple (Fantke et al., 2011b), and lettuce (Itoiz et al., 2012). Moreover, the analytical techniques are mainly not confirmatory, such as gas chromatography-electron capture detection (Fantke et al., 2011a).

Nevertheless, environment compartments and their characteristics in models are usually considered to remain constant (Fantke et al., 2011a). Thus, the models including dynamiCROP model are limited with respect to variable environmental conditions (Fantke et al., 2011a), such as temperature and precipitation.

Fortunately, the influence of temperature on pesticide dissipation in plants has recently been discussed in a sophisticated method which estimates pesticide dissipation half-lives based on substance properties, plant characteristics, and study conditions (Fantke et al., 2014). For example, Fantke et al. (2014) has found that 95% of the predicted half-lives are within a factor 4.5 of the reported half-lives taken from Fantke and Juraske (2013). However, the effect of precipitation on pesticide dissipation has not be addressed yet.

In this work, herbicides such as florasulam (PubChem CID: 11700495), carfentrazone-ethyl (PubChem CID: 86222), fluroxypyr (PubChem CID: 50465), and fluroxypyr-meptyl (PubChem CID: 54745) were selected as targets. DynamiCROP was applied to study environmental fate and behavior of four herbicides in wheat. Meantime, pesticide residues and dissipation half-lives were determined by field trials with application of real formulations, following good agricultural practice by our developed and confirmatory QuEChERS LC-MS/MS method. With the combination of field experiment and modelling. With the combination of field experiments and modelling, the black box of pesticide-plant-environment system was clarified. Furthermore, the following questions were answered based on both bottom up view and top down view of the plant-environment system, respectively. (1) Where did the residue come from? (2) Where did the pesticide go to? To push one step further, the influence of meteorological conditions on pesticide dissipation were investigated. To determine which condition was dominant, the contribution of temperature was quantified. Moreover, the predominant role of rain on pesticide dissipation were highlighted for the first time.

2. Materials and methods

2.1. Chemicals

Four standards were from commercial sources as available, florasulam (98.5%) from Jiangsu Agrochem Laboratory (Jiangsu, China), carfentrazone-ethyl (92.0%) from Beijing KeFaWeiYe Co. Ltd. (Beijing, China), fluroxypyr-meptyl (99.7%) from National Institute of Metrology China (Beijing, China), and fluroxypyr (97.0%) from Agro-Environmental Protection Institute Ministry of Agriculture (TianJing, China). Acetonitrile and formic acid from Fisher Scientific (Far Lawn, New Jersey) were of LC grade. Anhydrous magnesium sulphate ($MgSO_4$), sodium chloride (NaCl), and acetic acid of analytical grade were purchased from Beijing Chemical Reagents Company (Beijing, China). C18 (50 μm, 60 Å) and graphitized carfentrazone-ethylbon black (GCB) (120–400 mesh) were purchased from Agela Technologies (TianJing, China).