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Uptake kinetics and accumulation of pesticides in wheat (*Triticum aestivum L.*): Impact of chemical and plant properties

Qianyu Liu[a,b], Yingchao Liu[b], Fengshou Dong[a], J. Brett Sallach[c], Xiaohu Wu[a], Xingang Liu[a], Jun Xu[a], Yongquan Zheng[a] and Yuanbo Li[a]*

[a] Institute of Plant Protection, Chinese Academy of Agricultural Sciences, State Key Laboratory for Biology of Plant Diseases and Insect Pests, Beijing 100193, China

[b] College of Plant Protection, Hebei Agricultural University, Baoding 071000, PR China;

[c] Department of Environment and Geography, University of York, Heslington, York, YO10 5NG, United Kingdom

[*] Corresponding Author:

Dr. Yuanbo Li, Phone: 010-62815938. E-mail: liyuanbo@caas.cn

Abstract

Plant uptake is an important process in determining the transfer of pesticides through a food chain. Understanding how crops take up and translocate pesticides is critical in developing powerful models to predict pesticide accumulation in agricultural produce and potential human exposure. Herein, wheat was selected as a model plant species to investigate the uptake and distribution of eleven widely used pesticides in a hydroponic system as a function of time for 144 hours. The time-dependent uptake kinetics of these pesticides were fitted with a first-order 1-compartment kinetic model. During 144 hours, flusilazole and difenoconazole, with relative high log K_{ow} (3.87 and 4.36, respectively), displayed higher root uptake rate constants (k). To clarify the role of root lipid content (f_{lip}) in plant accumulation of pesticides, we conducted a lipid normalization meta-analysis using data from this and previous studies, and found that the f_{lip} value was an important factor in predicting the root concentration factor (RCF) of pesticides. An improved correlation was observed between log RCF and log $f_{lip}K_{ow}$ (R^2 = 0.748, N = 26, P < 0.001), compared with the correlation between log RCF and log K_{ow} (R^2 = 0.686, N = 26, P < 0.001). Furthermore, the hydrophilic pesticides (e.g. log K_{ow} < 2) were found to reach partition equilibrium faster than lipophilic pesticides (e.g. log K_{ow} > 3) during the uptake process. The quasi-equilibrium factor (α_{pt}) was inversely related to log K_{ow} (R^2 = 0.773, N = 11, P < 0.001) suggesting a hydrophobicity-regulated uptake equilibrium. Findings from this study could facilitate crop-uptake model optimization.

Capsule: Integrating the pesticide K_{ow} with plant root lipid content ($f_{lip}K_{ow}$) is better for predicting the root concentration factors of pesticides than just K_{ow}.

Keywords: Pesticides; Uptake kinetics; Root lipid content; Translocation; Root concentration factor.

1. Introduction

Food crops are exposed to various pesticides in agricultural systems as these chemicals are continuously applied to fields in order to promote crop productivity (Carvalho, 2006). Plant uptake is a key process governing the transfer of pesticides through the food chain. Obviously, a mechanistic understanding of how crops take up and accumulate pesticides from the surrounding environment (e.g., aqueous solution) is essential for the risk assessment of pesticide accumulation in agricultural products (Pullagurala et al., 2018). Data on plant uptake is essential in developing and parameterizing models to predict pesticide accumulation and subsequent human exposure through the terrestrial food chain (Gobas et al., 2016; Li et al., 2020; Wu and Zhu, 2019).

Once in soil, pesticides are transported into crops predominantly via root uptake and subsequently translocated to the other plant parts via the vascular system (Chiou et al., 2001; Su and Liang, 2015). Studies on the plant uptake of organic chemicals from hydroponic solution (or soil) have demonstrated that these chemicals enter plants predominately via passive (i.e., partition) processes (Briggs et al., 1982; Chiou

et al., 2001; Gao et al., 2005; Trapp, 2004). Passive uptake in crops could be considered as a series of pesticide partitions between the crop aqueous phase and crop organic components. Lipophilic compounds (i.e., high n-octanol–water partitioning coefficient, K_{ow}) have greater tendency to accumulate in plants than hydrophilic compounds (Li et al., 2019a). Strong positive linear correlations between plant bioaccumulation and K_{ow} have been well established to estimate the root uptake of organic chemicals (Briggs et al., 1982; Burken and Schnoor, 1998). Since the crop uptake process is a partition distribution between different tissues, lipids are considered to be a major reservoir for non-ionic organic compounds (Carter et al., 2014), especially for compounds with strong lipophilicity (e.g., log K_{ow} > 3.0), where these compounds mainly partition into lipid in local plant tissues (Collins et al., 2006; Liu et al., 2019). However, the critical role of lipids in understanding the plant accumulation of current-use pesticides is still not well explored.

Many studies have assumed plant uptake under quasi-equilibrium conditions (Briggs et al., 1982; Li et al., 2002). Chiou et al. (2001) formulated a partition-limited model to estimate the passive uptake of organic chemicals by plants from water or soil systems. During the uptake process, this model assumes the instantaneous local phase distribution equilibria of chemicals between plant compositions (e.g., carbohydrates and lipids) and sap water. These distribution processes lead to decreased chemical levels in sap water compared with that in external water, thus keeping the driving force for passive uptake and approaching the partition limit (e.g., equilibrium). A quasi-equilibrium factor (α_{pt}) is used to characterize the extent of equilibrium reached

between the plant interior and external water. As long as the α_{pt} value is obtained, it can then be used to estimate the concentration of a chemical in plants based on the water (or soil) concentrations and other relevant parameters. While this model has been verified by many studies on contaminant uptake by plants (Ju et al., 2020; Li et al., 2020), little is known about how the uptake kinetic process influences the α_{pt} value. Indeed, plant uptake of organic chemicals usually does not reach true equilibrium, therefore, uptake kinetics could help to estimate the degree of uptake reached at steady state. Information on time-dependent uptake of pesticides with a range of physicochemical properties and their temporal distribution in various plant tissues is needed for the further model optimization and application.

The aim of this study was to evaluate the uptake kinetics, translocation and bioaccumulation of 11 pesticides with diverse K_{ow} values (Table 1) in wheat seedlings grown in a hydroponic system. Wheat (*Triticum aestivum L.*) was selected to assess the plant uptake because this crop is potentially exposed to these pesticides directly or indirectly under field conditions. For example, triazole fungicides (triadimefon, tebuconazole, flusilazole and difenoconazole) are widely used to control wheat powdery mildew (Liang et al., 2013; Yerkovich et al., 2020; Zhang et al., 2015). Factors that may play important roles in pesticide uptake and distribution including K_{ow}, plant lipid content and uptake time were evaluated. The α_{pt} values, in terms of the partition-limited model, were also examined as a function of time. Results of this study could provide an increased understanding of plant accumulation of pesticides and facilitate the optimization of the crop-uptake model.

2 Materials and Methods

2.1 Chemicals

Eleven pesticides including imidacloprid, dimethoate, fosthiazate, pirimicarb, atrazine, chlorantraniliprole, ethoprophos, triadimefon, tebuconazole, flusilazole and difenoconazole were purchased from Dr. Ehrenstorfer (Germany, purity > 95%). Imidacloprid, dimethoate and pirimicarb are used to control wheat aphids (Neubauer et al., 1983; Niehoff and Poehling, 1995; Yuan et al., 2020); fosthiazate, chlorantraniliprole and ethoprophos are used to control soil nematodes (Huang et al., 2019; Leitão et al., 2014). HPLC grade acetonitrile (ACN) was obtained from Sigma Aldrich (Steinheim, Germany). Reagent-grade ACN, anhydrous magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl) were obtained from Beihua Fine-Chemicals Co. (Beijing, China). Graphitized carbon black (GCB, 40 μm), primary secondary amine (PSA, 40 μm), and 0.22-μm nylon syringe filters were purchased from Agela Technologies (Tianjin, China).

2.2 Wheat plant cultivation

Wheat seeds Zhengzhou 6389 were provided by Hebei agricultural university. These seeds were sterilized with a solution of 5 % sodium hypochlorite solution for 10 minutes, and then rinsed with deionized water. After imbibing in deionized water for 16 hours, the seeds were germinated in a polyvinyl chloride (PVC) seedling tray for 4 days. Then, the seedlings were transferred to a PVC box with 6 L of half-strength Hoagland solution. The nutrient elements in the Hoagland solution were

supplied at following concentrations: calcium nitrate tetrahydrate (945 mg/L), nitrate of potash (506 mg/L), ammonium nitrate (80 mg/L), potassium dihydrogen phosphate (136 mg/L), magnesium sulfate (493 mg/L), iron vitriol (5.56 g/L), EDTA•Na (7.46 g/L), potassium iodide (0.83 g/L), boric acid (6.2 mg/L), manganese sulfate (22.3 mg/L), zinc sulfate (8.6 mg/L), sodium molybdate (0.25 mg/L), copper sulfate (0.025 mg/L) and cobalt chloride (0.025 mg/L). The size of the box was 30 cm in length, 24 cm in width and 10 cm in height. The container was placed in a well-controlled growth chamber with the temperature of 25/20 °C (day/night) and 60 % humidity maintained. A 16:8 hr daily light cycle was conducted using fluorescent light with an intensity of 250 μmol m^{-2} s^{-1}. The hydroponic solution was changed every 2 days and the pH was maintained at 6.5.

2.3 Uptake kinetics of pesticides by wheat seedlings

After 14 days of growth, a total of 60 seedlings (root length of 15 ± 1 cm; shoot height of 20 ± 1 cm) were transferred into a PVC box containing 6 L of Hoagland solution with spiked pesticides. The wheat seedling roots were exposed to a mixture of 11 pesticides with individual concentrations of 100 ng/mL. Two control treatments were conducted including a wheat-free control (spiked solution only) to monitor the loss of pesticides and a pesticide-free control (wheat only). To avoid potential pesticide photolysis and minimize algal growth, the boxes were wrapped with aluminum foil and the gap between the lid and the wheat seedlings was filled with a sponge. Cultivation was similar as mentioned above. Six plants were taken out of the solution as one sample and three replicates were performed at time intervals of 2, 6,

12, 24, 48, 72, 96, 120 and 144 h. The plant samples were then rinsed with deionized water and divided into roots and shoots. The hydroponic solution was also sampled at the same time interval for the pesticide analysis. All the samples were stored at −20 °C prior to analysis.

2.4 Pesticide extraction and purification

Wheat shoots, roots and hydroponic solutions were extracted by a modified QuECHERS method. Specifically, for wheat plants, 2.0 g of roots or shoots (fresh weight) was thoroughly homogenized and placed in a 10-mL Teflon centrifuge tube, then 2 mL of acetonitrile was added and vortexed for 10 min. After that, 1.0 g of NaCl was added and vortexed for 5 min then centrifuged at 2588 *g* for 5 min. Next, 1 mL of supernatant was transferred to a 2-mL centrifuge tube including 150 mg of $MgSO_4$ and d-SPE sorbents (50 mg of PSA and 10 mg of GCB for shoot samples, and 50 mg of PSA for the root samples). The mixture was vigorously vortexed for 1 min and centrifuged at 2588 *g* for 5 min, and then the resulting supernatant was passed through a 0.22-μm nylon filter prior to LC/MS/MS analysis. For the hydroponic solution, 2 mL of water sample was extracted with 2 mL of acetonitrile. The mixture was vigorously vortexed for 10 min, and processed as described above except for the cleanup step (not required).

2.5 Determination the constituents of wheat roots

Fresh wheat roots were chopped into small pieces and freeze-dried for 48 hours. The root water content was calculated by the mass difference between the fresh sample and freeze-dried sample. Lipid content was determined by a slightly modified

177 previously published method (Wen et al., 2016). Briefly, 2.0 g of freeze-dried wheat
178 root was ground and Soxtec-extracted with 100 mL petroleum ether using solvent
179 extractors (SER148, Velp Scientifica, Usmate, Italy) at 180 ℃ for 3 h. After the
180 solvent was recovered and dried to a constant weight, the residue weight was recorded
181 as the wheat root lipid content. After accounting for water and lipids, the remaining
182 plant biomass was defined as the carbohydrate fraction of the wheat root.

183 *2.6 Instrument analysis*

184 The sample analysis was performed by a LC-MS/MS system consisting of a
185 Shimadzu prominence high-performance liquid chromatography (Columbia, MD,
186 USA) coupled to a AB-Sciex 5500 triple quadrupole mass spectrometer (Foster City,
187 CA, USA) in positive ionization mode (ESI+). The separation of target compounds
188 was achieved with a Bonshell-C_{18} column (50 mm × 2.1 mm, 2.7 μm) at 40 ℃.
189 Gradient elution was performed by the binary mobile phase consisting of 0.1 % (*v/v*)
190 formic acid in ultrapure water as phase A and acetonitrile as phase B. The injection
191 volume was 2 μL and the flow rate was 0.3 mL/min. The gradient program was set as
192 follows (with respect of phase A): 0 min, 90 % A, decreased to 10 % during 0-7.0 min,
193 held at 10 % during 7.0-8.0 min, then increased to 90 % during 8.0-8.1 min, with the
194 run complete at 10 min. Nitrogen gas (99.99 %) was used as the curtain gas, collision
195 gas and dry gas. The curtain gas interface adopted the method of reverse nitrogen
196 purging with low flow to increase the solvent atomization effect and greatly improved
197 the detection sensitivity. Curtain gas, collision gas and dry gas were set at 30 psi, 7 psi
198 and 50 psi, respectively. Ionspray voltage was set at 5500 V and the desolvation

199 temperature was maintained at 500 ℃. The ESI and MS parameters of eleven
200 pesticides were optimized individually to obtain the best quantification conditions.
201 The optimal MRM parameters are given in Table S1.

202 The recovery assays were performed to assess the effectiveness of the analytical
203 method for eleven pesticides in wheat tissues (roots and shoots) and solution samples.
204 The recoveries and RSDs of these pesticides in root, shoot and hydroponic solution
205 samples ranged from 75.27 % to 113.67 % (Table S2). Good linearity (R^2 > 0.9925)
206 was obtained for each pesticide in matrix-matched calibration curves (Table S3). The
207 method LOQ of the target pesticides is defined based on a signal-to-noise (S/N) of 10.
208 The method detection limits (MDL) was defined as S/N ratios greater or equal to 3,
209 and the results are presented in Table S4.

210 *2.7 Data processing and statistical analysis*

211 The uptake kinetics of pesticides by wheat were fitted with a first-order
212 1-compartment model,

213 $$C_{tissue}\,(t) = C_{tissue,eq}(1\text{-}e^{-kt}) \quad (1)$$

214 where C_{tissue} (t) is the concentration of pesticide in fresh plant tissue at time t,
215 $C_{tissue,eq}$ is the equilibrium tissue concentration, and k is uptake rate constant (per
216 hour).

217 Root concentration factor (RCF) and translocation factor (TF) were calculated
218 using the following two equations:

219 $$RCF = C_{root}/C_{water} \quad (2)$$

220 $$TF = C_{shoot}/C_{root} \quad (3)$$

where C_{root}, C_{shoot}, and C_{water} are the concentrations of each pesticide in root, shoot and solution samples, respectively, on a fresh weight basis (ng/g or ng/mL).

A quasi-equilibrium partition model proposed by Chiou in 2001, was employed to explore the relationships between the levels of pesticides in wheat plants and external water:

$$\alpha_{pt} = (C_{pt} / C_w)/[f_{pw} + f_{ch}K_{ch} + f_{lip}K_{lip}] \quad (4)$$

Where α_{pt} is the quasi-equilibrium factor, which describes the approach to equilibrium of a pesticide in a plant part between external water from the outside and water from plants as a function of time, with $\alpha_{pt} = 1$ denoting the equilibrium state. The magnitude of α_{pt} (≤ 1) is a determination of the extent to which equilibrium has been reached, which is associated with the pesticide partition coefficient (K_{ow}), plant components and uptake time. C_{pt} is the concentration of a pesticide in wheat roots on a fresh weight basis; C_w is the pesticide concentration in hydroponic solution; f_{pw}, f_{ch}, and f_{lip} are the weight percentages of water, carbohydrates and lipids in the root on the basis of fresh weight, K_{ch} and K_{lip} are the carbohydrate-water partition coefficient and the lipid-water partition coefficient, respectively. Statistical analysis of experimental results was conducted using Origin 2017 software for Windows (Origin Lab Corp., Northampton, MA, USA).

3 Results and Discussion

3.1 Uptake kinetics

Pharmacokinetic one-compartment models combined with first-order kinetics have been successfully used to describe the process of organic chemical uptake by plants from water (Muller et al., 2016; Zhou et al., 2020). In this study, the root uptake kinetics of 11 pesticides were fitted with a first-order 1-compartment kinetic model. Within 144 h of the uptake experiment, the concentration of pesticides in hydroponic solution remained relatively stable (Figure S1), with the variation less than 20 %. During 144 h exposure, the root uptake of dimethoate, fosthiazate, pirimicarb, atrazine, ethoprophos, triadimefon and tebuconazole reached stability within 96 h (Figure 1). The concentration of flusilazole and difenoconazole in wheat root increased sharply reaching steady state within 48 h. Among the 11 pesticides, the root uptake rate constant ($k_{1,\ root}$) was in the range of 0.001-0.699 h^{-1} (Table S5). Imidacloprid and chlorantraniliprole displayed the slowest $k_{1,\ root}$ value (0.001 h^{-1}), while difenoconazole exhibited the fastest uptake rate, with the $k_{1,\ root}$ values 0.699 h^{-1}, which was nearly 70 times greater than that of imidacloprid and chlorantraniliprole. The relatively fast root uptake rate of difenoconazole might be attributed to its high hydrophobicity (log K_{ow} = 4.36), which enables it to pass through the root cell membrane easily.

Pesticides can only enter the xylem through the symplast pathway and are then transported to the shoots (Miller et al., 2016; Su et al., 2010). The shoot concentration data of all studied pesticides were also fitted with 1-compartment kinetic model except for ethoprophos due to its substantial metabolism in shoots (Figure 1). Among the 10 pesticides, the shoot uptake rate constant ($k_{2,\ shoot}$) was in the range of

0.0003-0.120 h^{-1} (Figure 1, Table S5). The $k_{2, shoot}$ values of imidacloprid, fosthiazate, pirimicarb and atrazine were about 1.59-3.0 times higher than their $k_{1, root}$ values, indicating the faster translocation of these pesticides to the upward plant tissues through the xylem system after entering the root. On the other hand, the $k_{2, shoot}$ values of chlorantraniliprole, tebuconazole, flusilazole and difenoconazole were 2.2-31.8 smaller than those of $k_{1, root}$ values, suggesting the slower transport process of these compounds from root to shoot.

3.2 The impact of K_{ow} and root lipid on the RCF

During the uptake kinetic studies, 9 of 11 studied pesticides reached steady state, thus their RCF values were averaged during the steady state (48 (or 96 h) ─ 144 h). For imidacloprid and chlorantraniliprole, which did not reach steady state, their average RCF values were obtained using the data at 144 h of exposure. As shown in Figure S2, a weak positive relationship was observed between log RCF and log K_{ow} (R^2 = 0.363, N = 11, P = 0.049). The result was in agreement with the findings of previous studies (Briggs et al., 1982; Chiou et al., 2001; Ge et al., 2017; Li et al., 2019a).

The root accumulation of nonionized chemicals from hydroponic solution or soil pore water mainly consists of two key components: (i), the equilibrium between the concentration of the surrounding solution and the aqueous phases in plant roots; (ii), the partition of compounds to the root lipid components such as the cell membrane and cell wall (Li et al., 2019b). Therefore, plant root lipid is the other key factor in characterizing the plant accumulation of pesticides, especially for plants with

286 varied lipid contents (f_{lip}). In this study, the log K_{ow} values of the studied pesticides
287 ranged from 0.57 to 4.36. In order to better explore the relationship between RCF and
288 pesticide K_{ow} in different plant species and enhance the power of analysis, results
289 from this and five previous relevant studies were combined in a meta-analysis
290 (Beestman et al., 1969; Harris and Sans, 1967; Jiang et al., 2016; Mikes et al., 2009;
291 Trapp et al., 1990). The range of log K_{ow} was extended to 6.36 (e.g., DDT), and 6
292 other plant species were added in the analysis including carrot, radish, turnip, onion,
293 maize and barely. As shown in Figure 2A, a good positive linear correlation (R^2 =
294 0.686, N = 26, P < 0.001) was found between log RCF and log K_{ow} of the pesticides
295 in 7 plant species. Detailed data for the correlation analysis is given in Table S6. In
296 the seven plant species used for the correlation analysis, the root f_{lip} ranged from 0.1%
297 to 1.1%. Studies indicated that there was a positive correlation between the f_{lip} and
298 RCF for a same compound (e.g., phenanthrene and pyrene) in different plant species
299 (Collins et al., 2006; Gao and Zhu, 2004; Gao et al., 2005), indicating lipid-regulated
300 plant bioaccumuation. The f_{lip} was thus integrated as a parameter to correct the
301 correlation analysis. As expected, the correlation was improved (R^2 = 0.748, N = 26,
302 P < 0.001) with the inclusion of the f_{lip} (log RCF vs log $K_{ow}f_{lip}$) (Figure 2B), compared
303 with the correlation analysis without the input of f_{lip} (log RCF vs log K_{ow}) (Figure 2A).
304 However, few models with respect to plant uptake of organic chemicals have
305 considered the plant f_{lip} as an input parameter (Briggs et al., 1982; Li et al., 2005).
306 Therefore, the f_{lip} should be taken into account when developing a plant accumulation
307 model to enhance the predictive accuracy.

3.3 Translocation of pesticides from root to shoots

The ability of a pesticide to translocate from roots to shoots can be expressed as the translocation factor (TF). As presented in Figure S3, the TF values were averaged for all pesticides during 48-144 h of uptake, except for the TF value of ethoprophos which was averaged during 24-72 h, by considering the uptake equilibrium (Figure 1). The TF values of all pesticides were greater than 1 except for difenoconazole, indicating their preferential translocation from the underground to aboveground tissue. Difenoconazole demonstrated the lowest TF value (0.39), suggesting this pesticide tends to accumulate in the roots. Its relatively strong hydrophobicity may limit its translocation from roots to shoots.

For pesticides taken up by plant roots to reach the xylem system, they must travel across root epidermis, cortex and endodermis (Miller et al., 2016). Solute absorbed by the root hair must pass through at least one cell membrane in the endodermis via the symplastic pathway to the xylem (Foster and Miklavcic, 2016; Wang et al., 2019). Consequently, membrane permeability determined the ability of pesticides to translocate to plant shoots. The biomembrane permeability for nonionic chemicals is considered positively related to chemical lipophilicity (Collins et al., 2006). Neutral compounds with log K_{ow} values ranging from −1 to 5 are thought to mobile in the transpiration stream, and are expected to transport to shoots after they enter the xylem (Miller et al., 2016). In this study, log K_{ow} values of the studied pesticides (0.57-4.36) fall into this range. As shown in Figure 3A, when log TF values were plotted against log K_{ow} for all pesticides, a relatively poor negative correlation

was observed (R^2 = 0.515, N = 11, P = 0.013). This suggested that the hydrophobicity was not the singular driver of translocation processes of the investigated pesticides. Other factors may also contribute to translocation including molecular weight (MW), systematic activity and in planta-metabolism (Macherius et al., 2012; Sun et al., 2018). For example, MW is thought to be another factor that is associated with plant cell membrane permeability (Kumar and Gupta, 2016; Topp et al., 1986). Previous studies indicated that large-sized molecules (e.g., MW > 450 g/mol) experienced a slow diffusion rate through root cell membranes thus limiting their transport to the upward plant tissues (Chuang et al., 2019). In the current study, atrazine and chlorantraniliprole displayed similar log K_{ow} (2.71 and 2.86, respectively). However, the translocation of atrazine (TF = 5.6) was about 2.9 times greater than that of chlorantraniliprole (TF = 1.9). The MW of chlorantraniliprole (483.15 g/mol) is about 2.2 times higher than that of atrazine (215.68 g/mol). The relatively large-sized chlorantraniliprole molecule could limit its transport across the cell membrane before entering the xylem, therefore reducing its translocation to shoots compared to the smaller-sized atrazine. As shown in Figure 3B, when MW was employed as a parameter for the correlation analysis (log TF vs log K_{ow}MW), the linear correlation was greatly enhanced (R^2 = 0.720, N = 11, P < 0.001). Recently, Li et al. (2018) also found that the TF values of neonicotinoids in vegetables was negatively related to their MW. The results suggest that the compound hydrophobicity and MW may work collectively to control the translocation of pesticides from roots to shoots.

3.4 Dependence of Quasi-equilibrium factor (α_{pt}) on uptake time and chemical hydrophobicity

The partition-limited model treats the uptake process as a sequence of pesticide partitions between plant sap water and plant organic components (Chiou et al., 2001). In this study, the f_{pw}, f_{lip} and f_{ch} of wheat seedlings were 93.32, 0.57 and 6.11%, respectively. The quasi-equilibrium factor (α_{pt}) of the investigated pesticides was obtained based on these parameters as well as their concentrations in roots and hydroponic solution. The α_{pt} value was considered to be concentration-independent, and assumed to vary with the uptake time (Chiou et al., 2001). In this study, the changes of α_{pt} values in wheat roots as a function of time were presented in Figure 4. Generally, the α_{pt} values of all pesticides increased sharply initially and then maintained. In theory, the α_{pt} value will keep increasing with time until the uptake equilibrium (e.g, α_{pt} = 1) is achieved (Li et al., 2005). Whether the α_{pt} value of a pesticide could approach 1 over time was highly compound-dependent. For highly hydrophilic pesticides including imidacloprid, dimethoate, fosthiazate and pirimicarb (log K_{ow} < 2), their α_{pt} value increased sharply to approach 1 within 96 hours. For relatively lipophilic pesticides including triadimefon, tebuconazole, flusilazole and difenoconazole (log K_{ow} > 3), their α_{pt} value was still below 0.2 after 144 h of incubation. At the end of the experiment, the most water-soluble pesticide — imidacloprid (log K_{ow} = 0.57) exhibited the highest α_{pt} value while the most lipid-soluble — difenoconazole (log K_{ow} = 4.36) showed the lowest α_{pt} value.

To further understand the effects of pesticide hydrophobicity on their quasi-equilibrium factor in roots, the relationship between α_{pt} and log K_{ow} was analyzed for dimethoate, fosthiazate, pirimicarb, atrazine, ethoprophos, triadimefon tebuconazole flusilazole and difenoconazole with the average α_{pt} values during 96 — 144 h (stable stage), as well as imidacloprid and chlorantraniliprole at 144 h (the highest value). As shown in Figure 5, an inverse correlation was obtained between α_{pt} and log K_{ow} values ($R^2 = 0.773$, N = 11, $P < 0.001$). Yang and Zhu (2007) used the partition-limited model to predict polycyclic aromatic hydrocarbon uptake by ryegrass, and found the α_{pt} values of acenaphthene (0.230), fluorene (0.227), phenanthrene (0.172) and pyrene (0.146) decreased with increasing log K_{ow} (3.92-5.18). Gao et al. (2005) reported that the α_{pt} values of four compounds in ryegrass were in the order of lindane > phenanthrene > pyrene ≈ trifluralin, which was nearly the opposite order as their log K_{ow} values (3.72, 4.46, 4.88, and 5.34).

Overall, these results suggested that the variation of the in-plant pesticide level with time should be a function of the compound's partition capacity. For hydrophilic pesticides (e.g., log $K_{ow} < 2$), the in-plant level should approach steady-state in a shorter time than that of lipophilic pesticides (e.g., log $K_{ow} > 3$) during the uptake process.

4. Conclusions

Results from this study clearly showed that wheat was capable of taking up all the studied pesticides from hydroponic solution, but pesticides with different

hydrophobicity (log K_{ow}, 0.57 ─ 4.36) exhibited disparities in their uptake kinetics, bioaccumulation and quasi-equilibrium factors. The root lipid content was demonstrated to be an important parameter in optimizing the correlation between RCF and K_{ow} for pesticides in different plant species. By using $f_{lip}K_{ow}$ instead of K_{ow} to correct the root lipid effect on RCF, a more pronounced correlation was observed between log RCF and log $f_{lip}K_{ow}$ (R^2 = 0.748, N = 26, P < 0.001) than that between log RCF and log K_{ow} (R^2 = 0.686, N = 26, P < 0.001) for based on a meta-analysis of pesticide uptake in 7 plant species. All the studied pesticides had the potential to be translocated to the shoots (TF > 1) except difenoconazole (TF = 0.39), suggesting higher residues of these pesticides may be found in leafy vegetables such as cabbage and lettuce, although not investigated in the present study. Other than hydrophobicity, factors such as molecular weight may also influence the translocation processes. The water-soluble pesticides (e.g., log K_{ow} < 2) tend to reach uptake quasi-equilibrium faster than lipid-soluble pesticides (e.g., log K_{ow} > 3), and an inverse correlation was observed between quasi-equilibrium factor and pesticide hydrophobicity. These findings provide a better understanding of how plants accumulate pesticides and can be used to improve crop-uptake model development.

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Appendix A. Supplementary data

The following is the supplementary data to this article:

Instrument parameters, extract recoveries, matrix-matched calibrations, method detection limits, uptake kinetics parameters, data on the meta-analysis of the correlation between RCF and log K_{ow} (or log $K_{ow}f_{lip}$), and translocation factors.

References

Beestman, G.B., Keeney, D.R., Chesters, G., 1969. Dieldrin uptake by corn as affected by soil properties. Agron. J. 61, 247-250.

Briggs, G.G., Bromilow, R.H., Evans, A.A., 1982. Relationships between lipophilicity and root uptake and translocation of non-ionised chemicals by barley. Pest Manage. Sci. 13, 495-504.

Burken, J.G., Schnoor, J.L., 1998. Predictive relationships for uptake of organic contaminants by hybrid poplar trees. Environ. Sci. Technol. 32, 3379-3385.

Carter, L.J., Harris, E., Williams, M., Ryan, J.J., Kookana, R.S., Boxall, A.B., 2014. Fate and uptake of pharmaceuticals in soil-plant systems. J. Agric. Food Chem. 62, 816-825.

Carvalho, F.P., 2006. Agriculture, pesticides, food security and food safety. Environ. Sci. Policy. 9, 685-692.

Chen, J., Xia, X., Wang, H., Zhai, Y., Xi, N., Lin, H., Wen, W., 2019. Uptake pathway and accumulation of polycyclic aromatic hydrocarbons in spinach affected by warming in enclosed soil/water-air-plant microcosms. J. Hazard. Mater. 379, 120831.

Chiou, C.T., Sheng, G., Manes, M., 2001. A partition-limited model for the plant uptake of organic contaminants from soil and water. Environ. Sci. Technol. 35, 1437-1444.

Chuang, Y. H., Liu, C. H., Sallach, J.B., Hammerschmidt, R., Zhang, W., Boyd, S.A., Li, H., 2019. Mechanistic study on uptake and transport of pharmaceuticals in lettuce from water. Environ. Int. 131, 104976.

Collins, C., Fryer, M., Grosso, A., 2006. Plant uptake of non-ionic organic chemicals. Environ. Sci. Technol. 40, 45-52.

Foster, K.J., Miklavcic, S.J., 2016. Modeling root zone effects on preferred pathways for the passive transport of ions and water in plant roots. Front. Plant Sci. 7, 14.
Gao, Y., Zhu, L., 2004. Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils. Chemosphere 55, 1169-1178.
Gao, Y., Zhu, L., Ling, W., 2005. Application of the partition-limited model for plant uptake of organic chemicals from soil and water. Sci. Total Environ. 336, 171-182.
Ge, J., Cui, K., Yan, H.Q., Li, Y., Chai, Y.Y., Liu, X.J., Cheng, J.F., Yu, X.Y., 2017. Uptake and translocation of imidacloprid, thiamethoxam and difenoconazole in rice plants. Environ. Pollut. 226, 479-485.
Gobas, F.A., Burkhard, L.P., Doucette, W.J., Sappington, K.G., Verbruggen, E.M., Hope, B.K., Bonnell, M.A., Arnot, J.A., Tarazona, J.V., 2016. Review of existing terrestrial bioaccumulation models and terrestrial bioaccumulation modeling needs for organic chemicals. Integr. Environ. Assess. Manage. 12, 123-134.
Harris, C.R., Sans, W.W., 1967. Absorption of organochlorine insecticide residues from agricultural soils by root crops. J. Agric. Food Chem. 15, 861-863.
Huang, B., Wang, Q., Guo, M., Fang, W., Wang, X., Wang, Q., Yan, D., Ouyang, C., Li, Y., Cao, A., 2019. The synergistic advantage of combining chloropicrin or dazomet with fosthiazate nematicide to control root-knot nematode in cucumber production. J. Integr. Agric. 18, 2093-2106.
Jiang, L., Lin, J.L., Jia, L.X., Liu, Y., Pan, B., Yang, Y., Lin, Y., 2016. Effects of two different organic amendments addition to soil on sorption–desorption, leaching, bioavailability of penconazole and the growth of wheat (Triticum aestivum L.). J. Environ. Manage. 167, 130-138.
Ju, C., Zhang, H., Wu, R., Dong, S., Yao, S., Wang, F., Cao, D., Xu, S., Fang, H., Yu, Y., 2020. Upward translocation of acetochlor and atrazine in wheat plants depends on their distribution in roots. Sci. Total Environ. 703, 135636.
Kumar, K., Gupta, S.C., 2016. A Framework to predict uptake of trace organic compounds by plants. J. Environ. Qual. 45, 555-564.
Leitão, S., Moreira, M., Van, P.J., Ribeiro, R., José, M., Sousa, J.P., 2014. Ethoprophos fate on soil–water interface and effects on non-target terrestrial and aquatic biota under Mediterranean crop-based scenarios. Ecotoxicol. Environ. Saf. 103, 36-44.
Li, H., Sheng, G., Chiou, C.T., Xu, O., 2005. Relation of organic contaminant equilibrium sorption and kinetic uptake in plants. Environ. Sci. Technol. 39, 4864-4870.
Li, H., Sheng, G., Sheng, W., Xu, O., 2002. Uptake of trifluralin and lindane from water by ryegrass. Chemosphere 48, 335-341.
Li, Y., Chiou, C.T., Li, H., Schnoor, J.L., 2019a. Improved prediction of the bioconcentration factors of organic contaminants from soils into plant/crop roots by related physicochemical parameters. Environ. Int. 126, 46-53.
Li, Y., Long, L., Yan, H., Ge, J., Cheng, J., Ren, L., Yu, X., 2018. Comparison of uptake, translocation and accumulation of several neonicotinoids in komatsuna

(Brassica rapa var. perviridis) from contaminated soils. Chemosphere 200, 603-611.
Li, Y., Sallach, J.B., Zhang, W., Boyd, S.A., Li, H., 2019b. Insight into the distribution of pharmaceuticals in soil-water-plant systems. Water Res. 152, 38-46.
Li, Z., Wang, W., Zhu, L., 2020. A three-phase-successive partition-limited model to predict plant accumulation of organic contaminants from soils treated with surfactants. Environ. Pollut. 261, 114071.
Liang, H., Li, L., Qiu, J., Li, W., Yang, S., Zhou, Z., Qiu, L., 2013. Stereoselective transformation of triadimefon to metabolite triadimenol in wheat and soil under field conditions. J. Hazard. Mater. 260, 929-936.
Liu, Q., Wang, X., Yang, R., Yang, L., Sun, B., Zhu, L., 2019. Uptake kinetics, accumulation, and long-distance transport of organophosphate esters in plants: impacts of chemical and plant properties. Environ. Sci. Technol. 53, 4940-4947.
Macherius, A., Eggen, T., Lorenz, W., Moeder, M., Ondruschka, J., Reemtsma, T., 2012. Metabolization of the bacteriostatic agent triclosan in edible plants and its consequences for plant uptake assessment. Environ Sci Technol. 46, 10797-10804.
Mikes, O., Cupr, P., Trapp, S., Klanova, J., 2009. Uptake of polychlorinated biphenyls and organochlorine pesticides from soil and air into radishes (Raphanus sativus). Environ. Pollut. 157, 488-496.
Miller, E.L., Nason, S.L., Karthikeyan, K.G., Pedersen, J.A., 2016. Root uptake of pharmaceuticals and personal care product ingredients. Environ Sci Technol. 50, 525-541.
Muller, C.E., Lefevre, G.H., Timofte, A.E., Hussain, F., Sattely, E.S., Luthy, R.G., Chemistry, 2016. Competing mechanisms for perfluoroalkyl acid accumulation in plants revealed using an Arabidopsis model system. Environ. Toxicol. Chem. 35, 1138-1147.
Neubauer, I., Raccah, B., Aharonson, N., Swirski, E., Ishaaya, I., 1983. Systemic effect of aldicarb, dimethoate and ethiofencarb on mortality and population dynamics of the spirea aphid, Aphis citricola Van der Goot. Crop Prot. 2, 211-218.
Niehoff, B., Poehling, H.M., 1995. Population dynamics of aphids and syrphid larvae in winter wheat treated with different rates of pirimicarb. Agric., Ecosyst. Environ. 52, 51-55.
Pullagurala, V.L., Rawat, S., Adisa, I.O., Hernandez-Viezcas, J.A., Peralta-Videa, J.R., Gardea-Torresdey, J.L., 2018. Plant uptake and translocation of contaminants of emerging concern in soil. Sci. Total Environ. 636, 1585-1596.
Su, Y., Liang, Y., 2015. Foliar uptake and translocation of formaldehyde with Bracket plants (Chlorophytum comosum). J. Hazard. Mater. 291, 120-128.
Su, Y.H., Liu, T., Liang, Y.C., 2010. Transport via xylem of trichloroethylene in wheat, corn, and tomato seedlings. J. Hazard. Mater. 182, 472-476.

Sun, C., Dudley, S., McGinnis, M., Gan, J., 2018. Hydrogen peroxide mediates triclosan-induced inhibition of root growth in wheat seedlings. Environ. Pollut. 243, 472-479.

Topp, E., Scheunert, I., Attar, A., Korte, F., 1986. Factors affecting the uptake of 14C-labeled organic chemicals by plants from soil. Ecotoxicol. Environ. Saf. 11, 219-228.

Trapp, S., 2004. Plant uptake and transport models for neutral and ionic chemicals. Environ. Sci. Pollut. Res. 11, 33-39.

Trapp, S., Matthies, M., Scheunert, I., Topp, E.M., 1990. Modeling the bioconcentration of organic chemicals in plants. Environ. Sci. Technol. 24, 1246-1252.

Wang, W., Wan, Q., Li, Y., Xu, W., Yu, X., 2019. Uptake, translocation and subcellular distribution of pesticides in Chinese cabbage (Brassica rapa var. chinensis). Ecotoxicol. Environ. Saf. 183, 109488.

Wen, B., Wu, Y., Zhang, H., Liu, Y., Hu, X., Huang, H., Zhang, S., 2016. The roles of protein and lipid in the accumulation and distribution of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in plants grown in biosolids-amended soils. Environ. Pollut. 216, 682-688.

Wu, X., Zhu, L., 2019. Prediction of organic contaminant uptake by plants: modified partition-limited model based on a sequential ultrasonic extraction procedure. Environ. Pollut. 246, 124-130.

Yang, Z., Zhu, L., 2007. Performance of the partition-limited model on predicting ryegrass uptake of polycyclic aromatic hydrocarbons. Chemosphere 67, 402-409.

Yerkovich, N., Cantoro, R., Palazzini, J.M., Torres, A., Chulze, S.N., 2020. Fusarium head blight in Argentina: Pathogen aggressiveness, triazole tolerance and biocontrol-cultivar combined strategy to reduce disease and deoxynivalenol in wheat. Crop Prot. 137, 105300.

Yuan, W., Xu, B., Ran, G., Chen, H., Zhao, P., Huang, Q., 2020. Application of imidacloprid controlled-release granules to enhance the utilization rate and control wheat aphid on winter wheat. J. Integr. Agric. 19, 3045-3053.

Zhang, Z., Jiang, W., Jian, Q., Song, W., Zheng, Z., Wang, D., Liu, X., 2015. Residues and dissipation kinetics of triazole fungicides difenoconazole and propiconazole in wheat and soil in Chinese fields. Food Chem. 168, 396-403.

Zhou, J., Yang, Z., Liu, Q., Liu, Y., Liu, M., Wang, T., Zhu, L., 2020. Insights into uptake, tranlocation, and transformation mechanisms of perfluorophosphinates and perfluorophosphonates in wheat (*Triticum aestivum L.*). Environ. Sci. Technol. 54, 276-285.