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1	Uptake kinetics and accumulation of pesticides in wheat (Triticum
2	aestivum L.): Impact of chemical and plant properties
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23 Abstract

24 Plant uptake is an important process in determining the transfer of pesticides through 25 a food chain. Understanding how crops take up and translocate pesticides is critical in 26 developing powerful models to predict pesticide accumulation in agricultural produce 27 and potential human exposure. Herein, wheat was selected as a model plant species to 28 investigate the uptake and distribution of eleven widely used pesticides in a 29 hydroponic system as a function of time for 144 hours. The time-dependent uptake 30 kinetics of these pesticides were fitted with a first-order 1-compartment kinetic model. 31 During 144 hours, flusilazole and difenoconazole, with relative high log K_{ow} (3.87) 32 and 4.36, respectively), displayed higher root uptake rate constants (k). To clarify the 33 role of root lipid content (f_{lip}) in plant accumulation of pesticides, we conducted a 34 lipid normalization meta-analysis using data from this and previous studies, and found that the $f_{\rm lip}$ value was an important factor in predicting the root concentration factor 35 36 (RCF) of pesticides. An improved correlation was observed between log RCF and log $f_{\text{lip}}K_{\text{ow}}$ (R² = 0.748, N = 26, P < 0.001), compared with the correlation between log 37 38 RCF and log K_{ow} (R² = 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 39 lipophilic pesticides (e.g. log $K_{ow} > 3$) during the uptake process. The 40 quasi-equilibrium factor (α_{pt}) was inversely related to log K_{ow} (R² = 0.773, N = 11, P 41 42 < 0.001) suggesting a hydrophobicity-regulated uptake equilibrium. Findings from 43 this study could facilitate crop-uptake model optimization.

44

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

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

50

51 **1. Introduction**

52 Food crops are exposed to various pesticides in agricultural systems as these 53 chemicals are continuously applied to fields in order to promote crop productivity 54 (Carvalho, 2006). Plant uptake is a key process governing the transfer of pesticides 55 through the food chain. Obviously, a mechanistic understanding of how crops take up 56 and accumulate pesticides from the surrounding environment (e.g., aqueous solution) is essential for the risk assessment of pesticide accumulation in agricultural products 57 (Pullagurala et al., 2018). Data on plant uptake is essential in developing and 58 59 parameterizing models to predict pesticide accumulation and subsequent human 60 exposure through the terrestrial food chain (Gobas et al., 2016; Li et al., 2020; Wu 61 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 67 et al., 2001; Gao et al., 2005; Trapp, 2004). Passive uptake in crops could be 68 considered as a series of pesticide partitions between the crop aqueous phase and crop 69 organic components. Lipophilic compounds (i.e., high n-octanol-water partitioning 70 coefficient, K_{ow}) have greater tendency to accumulate in plants than hydrophilic 71 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 72 73 organic chemicals (Briggs et al., 1982; Burken and Schnoor, 1998). Since the crop uptake process is a partition distribution between different tissues, lipids are 7475 considered to be a major reservoir for non-ionic organic compounds (Carter et al., 76 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; 77 78 Liu et al., 2019). However, the critical role of lipids in understanding the plant 79 accumulation of current-use pesticides is still not well explored.

80 Many studies have assumed plant uptake under quasi-equilibrium conditions 81 (Briggs et al., 1982; Li et al., 2002). Chiou et al. (2001) formulated a partition-limited 82 model to estimate the passive uptake of organic chemicals by plants from water or soil 83 systems. During the uptake process, this model assumes the instantaneous local phase distribution equilibria of chemicals between plant compositions (e.g., carbohydrates 84 85 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 86 87 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 88

89 between the plant interior and external water. As long as the α_{pt} value is obtained, it 90 can then be used to estimate the concentration of a chemical in plants based on the 91 water (or soil) concentrations and other relevant parameters. While this model has 92 been verified by many studies on contaminant uptake by plants (Ju et al., 2020; Li et 93 al., 2020), little is known about how the uptake kinetic process influences the α_{pt} 94 value. Indeed, plant uptake of organic chemicals usually does not reach true 95 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 96 97 range of physicochemical properties and their temporal distribution in various plant 98 tissues is needed for the further model optimization and application.

99 The aim of this study was to evaluate the uptake kinetics, translocation and 100 bioaccumulation of 11 pesticides with diverse K_{ow} values (Table 1) in wheat seedlings 101 grown in a hydroponic system. Wheat (Triticum aestivum L.) was selected to assess 102 the plant uptake because this crop is potentially exposed to these pesticides directly or 103 indirectly under field conditions. For example, triazole fungicides (triadimefon, tebuconazole, flusilazole and difenoconazole) are widely used to control wheat 104 105 powdery mildew (Liang et al., 2013; Yerkovich et al., 2020; Zhang et al., 2015). 106 Factors that may play important roles in pesticide uptake and distribution including $K_{\rm ow}$, plant lipid content and uptake time were evaluated. The $\alpha_{\rm pt}$ values, in terms of 107 the partition-limited model, were also examined as a function of time. Results of this 108 109 study could provide an increased understanding of plant accumulation of pesticides and facilitate the optimization of the crop-uptake model. 110

112 **2 Materials and Methods**

113 2.1 Chemicals

Eleven pesticides including imidacloprid, dimethoate, fosthiazate, pirimicarb, 114 115 atrazine, chlorantraniliprole, ethoprophos, triadimefon, tebuconazole, flusilazole and 116 difenoconazole were purchased from Dr. Ehrenstorfer (Germany, purity > 95%). Imidacloprid, dimethoate and pirimicarb are used to control wheat aphids (Neubauer 117 et al., 1983; Niehoff and Poehling, 1995; Yuan et al., 2020); fosthiazate, 118 119 chlorantraniliprole and ethoprophos are used to control soil nematodes (Huang et al., 120 2019; Leitão et al., 2014). HPLC grade acetonitrile (ACN) was obtained from Sigma 121 Aldrich (Steinheim, Germany). Reagent-grade ACN, anhydrous magnesium sulfate 122 (MgSO₄) and sodium chloride (NaCl) were obtained from Beihua Fine-Chemicals Co. (Beijing, China). Graphitized carbon black (GCB, 40 µm), primary secondary amine 123 (PSA, 40 µm), and 0.22-µm nylon syringe filters were purchased from Agela 124 125 Technologies (Tianjin, China).

126 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

133	supplied at following concentrations: calcium nitrate tetrahydrate (945 mg/L), nitrate
134	of potash (506 mg/L), ammonium nitrate (80 mg/L), potassium dihydrogen phosphate
135	(136 mg/L), magnesium sulfate (493 mg/L), iron vitriol (5.56 g/L), EDTA•Na (7.46
136	g/L), potassium iodide (0.83 g/L), boric acid (6.2 mg/L), manganese sulfate (22.3
137	mg/L), zinc sulfate (8.6 mg/L), sodium molybdate (0.25 mg/L), copper sulfate (0.025
138	mg/L) and cobalt chloride (0.025 mg/L). The size of the box was 30 cm in length, 24
139	cm in width and 10 cm in height. The container was placed in a well-controlled
140	growth chamber with the temperature of 25/20 $^{\circ}\mathrm{C}$ (day/night) and 60 % humidity
141	maintained. A 16:8 hr daily light cycle was conducted using fluorescent light with an
142	intensity of 250 μ mol m ⁻² s ⁻¹ . The hydroponic solution was changed every 2 days and
143	the pH was maintained at 6.5.

144 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 145 height of 20 ± 1 cm) were transferred into a PVC box containing 6 L of Hoagland 146 solution with spiked pesticides. The wheat seedling roots were exposed to a mixture 147 of 11 pesticides with individual concentrations of 100 ng/mL. Two control treatments 148 were conducted including a wheat-free control (spiked solution only) to monitor the 149 loss of pesticides and a pesticide-free control (wheat only). To avoid potential 150 pesticide photolysis and minimize algal growth, the boxes were wrapped with 151152aluminum 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 153154 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.

159 2.4 Pesticide extraction and purification

160 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 161 weight) was thoroughly homogenized and placed in a 10-mL Teflon centrifuge tube, 162 163 then 2 mL of acetonitrile was added and vortexed for 10 min. After that, 1.0 g of NaCl 164 was added and vortexed for 5 min then centrifuged at 2588 g for 5 min. Next, 1 mL of 165 supernatant was transferred to a 2-mL centrifuge tube including 150 mg of MgSO₄ 166 and d-SPE sorbents (50 mg of PSA and 10 mg of GCB for shoot samples, and 50 mg 167 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 168 a 0.22-µm nylon filter prior to LC/MS/MS analysis. For the hydroponic solution, 2 169 170mL 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 171 172 cleanup step (not required).

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

183 2.6 Instrument analysis

The sample analysis was performed by a LC-MS/MS system consisting of a 184 185 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-C₁₈ column (50 mm \times 2.1 mm, 2.7 µm) at 40 °C. 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 purging with low flow to increase the solvent atomization effect and greatly improved 196 the detection sensitivity. Curtain gas, collision gas and dry gas were set at 30 psi, 7 psi 197 198 and 50 psi, respectively. Ionspray voltage was set at 5500 V and the desolvation

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

The recovery assays were performed to assess the effectiveness of the analytical 202 203 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 samples ranged from 75.27 % to 113.67 % (Table S2). Good linearity ($R^2 > 0.9925$) 205 was obtained for each pesticide in matrix-matched calibration curves (Table S3). The 206 207 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

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

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

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

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

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

220
$$TF = C_{shoot}/C_{root}$$
(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:

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

Where α_{pt} is the quasi-equilibrium factor, which describes the approach to 227 228 equilibrium of a pesticide in a plant part between external water from the outside and 229 water from plants as a function of time, with $\alpha_{pt} = 1$ denoting the equilibrium state. 230 The magnitude of α_{pt} (≤ 1) is a determination of the extent to which equilibrium has 231 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 232 a fresh weight basis; C_w is the pesticide concentration in hydroponic solution; f_{pw} , f_{ch} , 233 and $f_{\rm lip}$ are the weight percentages of water, carbohydrates and lipids in the root on the 234 235basis 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 236 237 results was conducted using Origin 2017 software for Windows (Origin Lab Corp., 238 Northampton, MA, USA).

239

240 **3 Results and Discussion**

241 3.1 Uptake kinetics

242 Pharmacokinetic one-compartment models combined with first-order kinetics 243 have been successfully used to describe the process of organic chemical uptake by 244 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 245 246 model. Within 144 h of the uptake experiment, the concentration of pesticides in 247 hydroponic solution remained relatively stable (Figure S1), with the variation less than 20 %. During 144 h exposure, the root uptake of dimethoate, fosthiazate, 248 pirimicarb, atrazine, ethoprophos, triadimefon and tebuconazole reached stability 249 250 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 251 root uptake rate constant ($k_{1, root}$) was in the range of 0.001-0.699 h⁻¹ (Table S5). 252 253Imidacloprid 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, 254which was nearly 70 times greater than that of imidacloprid and chlorantraniliprole. 255The relatively fast root uptake rate of difenoconazole might be attributed to its high 256 hydrophobicity (log $K_{ow} = 4.36$), which enables it to pass through the root cell 257 258 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 264 0.0003-0.120 h⁻¹ (Figure 1, Table S5). The $k_{2, shoot}$ values of imidacloprid, fosthiazate, 265 pirimicarb and atrazine were about 1.59-3.0 times higher than their $k_{1, root}$ values, 266 indicating the faster translocation of these pesticides to the upward plant tissues 267 through the xylem system after entering the root. On the other hand, the $k_{2, shoot}$ values 268 of chlorantraniliprole, tebuconazole, flusilazole and difenoconazole were 2.2-31.8 269 smaller than those of $k_{1, root}$ values, suggesting the slower transport process of these 270 compounds from root to shoot.

271 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 272 state, thus their RCF values were averaged during the steady state (48 (or 96 h) - 144 273 274 h). For imidacloprid and chlorantraniliprole, which did not reach steady state, their 275 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} 276 $(R^2 = 0.363, N = 11, P = 0.049)$. The result was in agreement with the findings of 277 278 previous studies (Briggs et al., 1982; Chiou et al., 2001; Ge et al., 2017; Li et al., 279 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 from this and five previous relevant studies were combined in a meta-analysis 289 290 (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, maize and barely. As shown in Figure 2A, a good positive linear correlation ($R^2 =$ 293 294 0.686, N = 26, $P \le 0.001$) 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 $f_{\rm lip}$ 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 correlation analysis. As expected, the correlation was improved ($R^2 = 0.748$, N = 26, 301 302 P < 0.001) with the inclusion of the f_{lip} (log RCF vs log $K_{\text{ow}}f_{\text{lip}}$) (Figure 2B), compared with the correlation analysis without the input of f_{lip} (log RCF vs log K_{ow}) (Figure 2A). 303 304 However, few models with respect to plant uptake of organic chemicals have considered the plant fip as an input parameter (Briggs et al., 1982; Li et al., 2005). 305 306 Therefore, the f_{lip} should be taken into account when developing a plant accumulation model to enhance the predictive accuracy. 307

308 3.3 Translocation of pesticides from root to shoots

309 The ability of a pesticide to translocate from roots to shoots can be expressed as 310 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 311 312 which was averaged during 24-72 h, by considering the uptake equilibrium (Figure 1). 313 The TF values of all pesticides were greater than 1 except for difenoconazole, 314 indicating their preferential translocation from the underground to aboveground tissue. Difenoconazole demonstrated the lowest TF value (0.39), suggesting this pesticide 315 316 tends to accumulate in the roots. Its relatively strong hydrophobicity may limit its 317 translocation from roots to shoots.

318 For pesticides taken up by plant roots to reach the xylem system, they must 319 travel across root epidermis, cortex and endodermis (Miller et al., 2016). Solute 320 absorbed by the root hair must pass through at least one cell membrane in the 321 endodermis via the symplastic pathway to the xylem (Foster and Miklavcic, 2016; 322 Wang et al., 2019). Consequently, membrane permeability determined the ability of 323 pesticides to translocate to plant shoots. The biomembrane permeability for nonionic 324 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 325 326 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 327 328 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 329

330	was observed ($R^2 = 0.515$, $N = 11$, $P = 0.013$). This suggested that the hydrophobicity
331	was not the singular driver of translocation processes of the investigated pesticides.
332	Other factors may also contribute to translocation including molecular weight (MW),
333	systematic activity and in planta-metabolism (Macherius et al., 2012; Sun et al., 2018).
334	For example, MW is thought to be another factor that is associated with plant cell
335	membrane permeability (Kumar and Gupta, 2016; Topp et al., 1986). Previous studies
336	indicated that large-sized molecules (e.g., MW > 450 g/mol) experienced a slow
337	diffusion rate through root cell membranes thus limiting their transport to the upward
338	plant tissues (Chuang et al., 2019). In the current study, atrazine and
339	chlorantraniliprole displayed similar log K_{ow} (2.71 and 2.86, respectively). However,
340	the translocation of atrazine (TF = 5.6) was about 2.9 times greater than that of
341	chlorantraniliprole (TF = 1.9). The MW of chlorantraniliprole (483.15 g/mol) is about
342	2.2 times higher than that of atrazine (215.68 g/mol). The relatively large-sized
343	chlorantraniliprole molecule could limit its transport across the cell membrane before
344	entering the xylem, therefore reducing its translocation to shoots compared to the
345	smaller-sized atrazine. As shown in Figure 3B, when MW was employed as a
346	parameter for the correlation analysis (log TF vs log $K_{ow}MW$), the linear correlation
347	was greatly enhanced ($R^2 = 0.720$, $N = 11$, $P < 0.001$). Recently, Li et al. (2018) also
348	found that the TF values of neonicotinoids in vegetables was negatively related to
349	their MW. The results suggest that the compound hydrophobicity and MW may work
350	collectively to control the translocation of pesticides from roots to shoots.

351 3.4 Dependence of Quasi-equilibrium factor (α_{pt}) on uptake time and chemical
352 hydrophobicity

353 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). 354 355 In this study, the f_{pw} , f_{lip} and f_{ch} of wheat seedlings were 93.32, 0.57 and 6.11%, 356 respectively. The quasi-equilibrium factor (α_{pt}) of the investigated pesticides was 357 obtained based on these parameters as well as their concentrations in roots and 358 hydroponic solution. The α_{pt} value was considered to be concentration-independent, 359 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. 360 Generally, the α_{pt} values of all pesticides increased sharply initially and then 361 362 maintained. In theory, the α_{pt} value will keep increasing with time until the uptake equilibrium (e.g, $\alpha_{pt} = 1$) is achieved (Li et al., 2005). Whether the α_{pt} value of a 363 364 pesticide could approach 1 over time was highly compound-dependent. For highly 365 hydrophilic pesticides including imidacloprid, dimethoate, fosthiazate and pirimicarb 366 (log $K_{ow} < 2$), their α_{pt} value increased sharply to approach 1 within 96 hours. For 367 relatively lipophilic pesticides including triadimefon, tebuconazole, flusilazole and 368 difenoconazole (log $K_{ow} > 3$), their α_{pt} value was still below 0.2 after 144 h of 369 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 370 371 lipid-soluble – difenoconazole (log $K_{ow} = 4.36$) showed the lowest α_{pt} value.

372	To further understand the effects of pesticide hydrophobicity on their
373	quasi-equilibrium factor in roots, the relationship between α_{pt} and log K_{ow} was
374	analyzed for dimethoate, fosthiazate, pirimicarb, atrazine, ethoprophos, triadimefon
375	tebuconazole flusilazole and difenoconazole with the average α_{pt} values during 96 –
376	144 h (stable stage), as well as imidacloprid and chlorantraniliprole at 144 h (the
377	highest value). As shown in Figure 5, an inverse correlation was obtained between α_{pt}
378	and log K_{ow} values (R ² = 0.773, N = 11, $P \le 0.001$). Yang and Zhu (2007) used the
379	partition-limited model to predict polycyclic aromatic hydrocarbon uptake by ryegrass,
380	and found the α_{pt} values of acenaphthene (0.230), fluorene (0.227), phenanthrene
381	(0.172) and pyrene (0.146) decreased with increasing log K_{ow} (3.92-5.18). Gao et al.
382	(2005) reported that the α_{pt} values of four compounds in ryegrass were in the order of
383	lindane > phenanthrene > pyrene \approx trifluralin, which was nearly the opposite order as
384	their log <i>K</i> _{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.

390

391 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

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

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- 418 Appendix A. Supplementary data
- 419 The following is the supplementary data to this article:
- 420 Instrument parameters, extract recoveries, matrix-matched calibrations, method
- 421 detection limits, uptake kinetics parameters, data on the meta-analysis of the
- 422 correlation between RCF and log K_{ow} (or log $K_{ow} f_{lip}$), and translocation factors.
- 423

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