

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
35 that the f_{lip} value was an important factor in predicting the root concentration factor
36 (RCF) of pesticides. An improved correlation was observed between \log RCF and \log
37 $f_{lip}K_{ow}$ ($R^2 = 0.748$, $N = 26$, $P < 0.001$), compared with the correlation between \log
38 RCF and $\log K_{ow}$ ($R^2 = 0.686$, $N = 26$, $P < 0.001$). Furthermore, the hydrophilic
39 pesticides (e.g. $\log K_{ow} < 2$) were found to reach partition equilibrium faster than
40 lipophilic pesticides (e.g. $\log K_{ow} > 3$) during the uptake process. The
41 quasi-equilibrium factor (α_{pt}) was inversely related to $\log K_{ow}$ ($R^2 = 0.773$, $N = 11$, P
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} .

47

48 *Keywords:* Pesticides; Uptake kinetics; Root lipid content; Translocation; Root
49 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)
57 is essential for the risk assessment of pesticide accumulation in agricultural products
58 (Pullagurala et al., 2018). Data on plant uptake is essential in developing and
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).

62 Once in soil, pesticides are transported into crops predominantly via root uptake
63 and subsequently translocated to the other plant parts via the vascular system (Chiou
64 et al., 2001; Su and Liang, 2015). Studies on the plant uptake of organic chemicals
65 from hydroponic solution (or soil) have demonstrated that these chemicals enter
66 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
72 bioaccumulation and K_{ow} have been well established to estimate the root uptake of
73 organic chemicals (Briggs et al., 1982; Burken and Schnoor, 1998). Since the crop
74 uptake process is a partition distribution between different tissues, lipids are
75 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
77 these compounds mainly partition into lipid in local plant tissues (Collins et al., 2006;
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
84 distribution equilibria of chemicals between plant compositions (e.g., carbohydrates
85 and lipids) and sap water. These distribution processes lead to decreased chemical
86 levels in sap water compared with that in external water, thus keeping the driving
87 force for passive uptake and approaching the partition limit (e.g., equilibrium). A
88 quasi-equilibrium factor (α_{pt}) is used to characterize the extent of equilibrium reached

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
96 reached at steady state. Information on time-dependent uptake of pesticides with a
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,
104 tebuconazole, flusilazole and difenoconazole) are widely used to control wheat
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
107 K_{ow} , plant lipid content and uptake time were evaluated. The α_{pt} values, in terms of
108 the partition-limited model, were also examined as a function of time. Results of this
109 study could provide an increased understanding of plant accumulation of pesticides
110 and facilitate the optimization of the crop-uptake model.

111

112 **2 Materials and Methods**

113 *2.1 Chemicals*

114 Eleven pesticides including imidacloprid, dimethoate, fosthiazate, pirimicarb,
115 atrazine, chlorantraniliprole, ethoprophos, triadimefon, tebuconazole, flusilazole and
116 difenoconazole were purchased from Dr. Ehrenstorfer (Germany, purity > 95%).
117 Imidacloprid, dimethoate and pirimicarb are used to control wheat aphids (Neubauer
118 et al., 1983; Niehoff and Poehling, 1995; Yuan et al., 2020); fosthiazate,
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.
123 (Beijing, China). Graphitized carbon black (GCB, 40 μm), primary secondary amine
124 (PSA, 40 μm), and 0.22-μm nylon syringe filters were purchased from Agela
125 Technologies (Tianjin, China).

126 *2.2 Wheat plant cultivation*

127 Wheat seeds Zhengzhou 6389 were provided by Hebei agricultural university.
128 These seeds were sterilized with a solution of 5 % sodium hypochlorite solution for
129 10 minutes, and then rinsed with deionized water. After imbibing in deionized water
130 for 16 hours, the seeds were germinated in a polyvinyl chloride (PVC) seedling tray
131 for 4 days. Then, the seedlings were transferred to a PVC box with 6 L of
132 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 °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 $\mu\text{mol m}^{-2} \text{s}^{-1}$. 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*

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

155 12, 24, 48, 72, 96, 120 and 144 h. The plant samples were then rinsed with deionized
156 water and divided into roots and shoots. The hydroponic solution was also sampled at
157 the same time interval for the pesticide analysis. All the samples were stored at
158 $-20\text{ }^{\circ}\text{C}$ prior to analysis.

159 *2.4 Pesticide extraction and purification*

160 Wheat shoots, roots and hydroponic solutions were extracted by a modified
161 QuECHERS method. Specifically, for wheat plants, 2.0 g of roots or shoots (fresh
162 weight) was thoroughly homogenized and placed in a 10-mL Teflon centrifuge tube,
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 MgSO_4
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
168 centrifuged at 2588 g for 5 min, and then the resulting supernatant was passed through
169 a 0.22- μm nylon filter prior to LC/MS/MS analysis. For the hydroponic solution, 2
170 mL of water sample was extracted with 2 mL of acetonitrile. The mixture was
171 vigorously vortexed for 10 min, and processed as described above except for the
172 cleanup step (not required).

173 *2.5 Determination the constituents of wheat roots*

174 Fresh wheat roots were chopped into small pieces and freeze-dried for 48 hours.
175 The root water content was calculated by the mass difference between the fresh
176 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 °C 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-C₁₈ column (50 mm × 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
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 °C. 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,

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

214 where $C_{\text{tissue}}(t)$ is the concentration of pesticide in fresh plant tissue at time t ,
215 $C_{\text{tissue,eq}}$ 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:

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

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

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

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

$$226 \quad \alpha_{\text{pt}} = (C_{\text{pt}} / C_{\text{w}}) / [f_{\text{pw}} + f_{\text{ch}}K_{\text{ch}} + f_{\text{lip}}K_{\text{lip}}] \quad (4)$$

227 Where α_{pt} is the quasi-equilibrium factor, which describes the approach to
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 $\alpha_{\text{pt}} = 1$ 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
232 components and uptake time. C_{pt} is the concentration of a pesticide in wheat roots on
233 a fresh weight basis; C_{w} is the pesticide concentration in hydroponic solution; f_{pw} , f_{ch} ,
234 and f_{lip} are the weight percentages of water, carbohydrates and lipids in the root on the
235 basis of fresh weight, K_{ch} and K_{lip} are the carbohydrate-water partition coefficient and
236 the lipid-water partition coefficient, respectively. Statistical analysis of experimental
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
245 uptake kinetics of 11 pesticides were fitted with a first-order 1-compartment kinetic
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
248 than 20 %. During 144 h exposure, the root uptake of dimethoate, fosthiazate,
249 pirimicarb, atrazine, ethoprophos, triadimefon and tebuconazole reached stability
250 within 96 h (Figure 1). The concentration of flusilazole and difenoconazole in wheat
251 root increased sharply reaching steady state within 48 h. Among the 11 pesticides, the
252 root uptake rate constant ($k_{1, \text{root}}$) was in the range of 0.001-0.699 h⁻¹ (Table S5).
253 Imidacloprid and chlorantraniliprole displayed the slowest $k_{1, \text{root}}$ value (0.001 h⁻¹),
254 while difenoconazole exhibited the fastest uptake rate, with the $k_{1, \text{root}}$ values 0.699 h⁻¹,
255 which was nearly 70 times greater than that of imidacloprid and chlorantraniliprole.
256 The relatively fast root uptake rate of difenoconazole might be attributed to its high
257 hydrophobicity ($\log K_{\text{ow}} = 4.36$), which enables it to pass through the root cell
258 membrane easily.

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

264 0.0003-0.120 h⁻¹ (Figure 1, Table S5). The $k_{2, \text{shoot}}$ values of imidacloprid, fosthiazate,
265 pirimicarb and atrazine were about 1.59-3.0 times higher than their $k_{1, \text{root}}$ 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 $k_{2, \text{shoot}}$ values
268 of chlorantraniliprole, tebuconazole, flusilazole and difenoconazole were 2.2-31.8
269 smaller than those of $k_{1, \text{root}}$ 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*

272 During the uptake kinetic studies, 9 of 11 studied pesticides reached steady
273 state, thus their RCF values were averaged during the steady state (48 (or 96 h) – 144
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
276 Figure S2, a weak positive relationship was observed between log RCF and log K_{ow}
277 ($R^2 = 0.363$, $N = 11$, $P = 0.049$). The result was in agreement with the findings of
278 previous studies (Briggs et al., 1982; Chiou et al., 2001; Ge et al., 2017; Li et al.,
279 2019a).

280 The root accumulation of nonionized chemicals from hydroponic solution or
281 soil pore water mainly consists of two key components: (i), the equilibrium between
282 the concentration of the surrounding solution and the aqueous phases in plant roots;
283 (ii), the partition of compounds to the root lipid components such as the cell
284 membrane and cell wall (Li et al., 2019b). Therefore, plant root lipid is the other key
285 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 bioaccumulation. 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.

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
311 for all pesticides during 48-144 h of uptake, except for the TF value of ethoprophos
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.
315 Difenoconazole demonstrated the lowest TF value (0.39), suggesting this pesticide
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.,
325 2006). Neutral compounds with $\log K_{ow}$ values ranging from -1 to 5 are thought to
326 mobile in the transpiration stream, and are expected to transport to shoots after they
327 enter the xylem (Miller et al., 2016). In this study, $\log K_{ow}$ values of the studied
328 pesticides (0.57-4.36) fall into this range. As shown in Figure 3A, when $\log TF$ values
329 were plotted against $\log K_{ow}$ for all pesticides, a relatively poor negative correlation

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
354 partitions between plant sap water and plant organic components (Chiou et al., 2001).
355 In this study, the f_{pw} , f_{ip} 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
360 changes of α_{pt} values in wheat roots as a function of time were presented in Figure 4.
361 Generally, the α_{pt} values of all pesticides increased sharply initially and then
362 maintained. In theory, the α_{pt} value will keep increasing with time until the uptake
363 equilibrium (e.g, $\alpha_{pt} = 1$) is achieved (Li et al., 2005). Whether the α_{pt} value of a
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 —
370 imidacloprid ($\log K_{ow} = 0.57$) exhibited the highest α_{pt} value while the most
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 ($R^2 = 0.773$, $N = 11$, $P < 0.001$). 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 $\log K_{ow}$ values (3.72, 4.46, 4.88, and 5.34).

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

390

391 **4. Conclusions**

392 Results from this study clearly showed that wheat was capable of taking up all
393 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.

411

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417

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 $\log K_{ow/fip}$), and translocation factors.

423

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