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1 **Measured and modeled residue dynamics of famoxadone and oxathiapiprolin in tomato fields**

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14 ABSTRACT: A reliable analytical method for the simultaneous determination of famoxadone and
15 oxathiapiprolin dissipation kinetics, as well as the metabolites of oxathiapiprolin (IN-E8S72 and
16 IN-WR791) in tomato and soil was developed. We studied the dissipation of famoxadone and
17 oxathiapiprolin in tomatoes grown using different kinetic curves in the area of Beijing in 2015 and
18 2016. Our results show that the most suitable model for two fungicides in 2015 and 2016 was
19 first-order kinetic and second-order kinetic with the half-lives 3.4 to 5.2 and 2.4 to 3.0 days,
20 respectively. In addition, we applied the dynamic plant uptake model dynamiCROP and combined it
21 with results from the field experiments to investigate the uptake and translocation of famoxadone and
22 oxathiapiprolin in the soil-tomato environment. Modeled and measured results of two years fitted well
23 with R^2 values ranging from 0.8072 to 0.9221. The fractions of famoxadone and oxathiapiprolin
24 applied during tomato cultivation that are eventually ingested by humans via residues in crop harvest
25 were finally evaluated and found to be in the range of one part per thousand, that is one gram intake per
26 kg applied.

27

28 Keywords: dissipation; pesticides; plant uptake model; dynamiCROP; half-life

29

30

31 **INTRODUCTION**

32 With a global production of 172 million tons in 2014 and an increase of 35% between 2004 and
33 2014, tomato is one of the most important vegetable crops in regard to human consumption.¹ The fruits
34 rich in nutrients can be eaten uncooked or cooked and processed as e.g. ketchup, juice, and puree.² In
35 order to increase yield of tomatoes and to control unwanted pests and diseases, pesticides are
36 continuously and intensively applied in tomato agroecosystems.³ However, humans may inhale and
37 ingest pesticides that reach non-target areas through wind drift, surface runoff, leaching, and
38 bystander.⁴ More importantly, pesticide residues in vegetables through consumption may lead to higher
39 exposure for human.^{5,6} In particular, tomatoes are usually less processed before consumed. Maximum
40 Residue Limits (MRLs) have been established by several national monitoring organizations (e.g.,
41 European Commission and Codex Alimentarius Commission) to reduce human exposure dose to
42 pesticides and ensure that the consumption of crop products is within acceptable risk levels. However,
43 MRLs of major pesticides are often established based on limits of determination (LOD) and acceptable
44 daily intake (ADI). The understanding of pesticide distribution in the environment and potential
45 toxicity-related effects on humans, in contrast, are usually not considered. Due to the extreme
46 complexity of consistently characterizing the crop-environment system including the consideration of
47 crop characteristics, substance properties and environmental properties, it is a challenging task to fully
48 understand the behavior of pesticides in agricultural fields and subsequent exposures and impacts on
49 humans and the environment.^{7,8}

50 A number of studies on the dissipation of pesticides in the crops have been reported.⁹⁻¹³ However,
51 most of these studies only focus on the pesticide residue values in the environment (e.g., soil and water)
52 and the behavior of pesticides, such as pesticide uptake and translocation processes in the plants grown

53 for human or animal consumption, has not been explained. Besides, pesticides dissipation evaluation is
54 measured by analytical methods which often limited by the time involved, high costs and analytical
55 detection limits.¹⁴ In order to address these gaps, a variety of models have been developed to predict
56 dissipation trend of pesticide in crops and provide deeper insights into specific plant-environment
57 systems since the 1990s. A detailed review was reported by Fantke et al. in 2011.¹⁵ Some of these
58 models were developed only for pesticide uptake and transfer through roots and tubers,^{16,17} while some
59 only focused on atmospheric deposition onto leaves.¹⁸ Roots, stem, leaves, fruits, and soil were all
60 considered as compartments in studies by Rein et al.¹⁹ and Legind et al.²⁰ However, the parameter of air
61 was not included in their models.

62 Recently, a dynamic plant-uptake model, named dynamiCROP, was developed by Fantke et al.
63 ^{8,15,21} The dynamiCROP model includes all compartments (environmental and plant compartments) and
64 pathways (pesticide initial mass distribution, bioaccumulation, and translocation) for assessing
65 pesticide uptake into crops, and subsequent human health and ecosystem health exposures and impacts.
66 More importantly, the model includes nine major food crops (wheat, rice, barley, maize, tomato, apple,
67 potato, lettuce, and passion fruit) consumed by humans in daily life and has been successfully applied
68 to predict some pesticide residues in wheat, rice, potato, apple, passion fruit, lettuces and
69 tomatoes.^{8,15,22-25}

70 Famoxadone and oxathiapiprolin were two fungicide widely used in tomatoes.²⁶⁻²⁸ Especially for
71 oxathiapiprolin, discovered and developed by DuPont in July 2012, is the first piperidinyl thiazole
72 isoxazoline fungicide.²⁶ IN-E8S72 and IN-WR791 are the two metabolites of it. There were no relevant
73 reports for the residue concentration and the process of dynamic dissipation of two compounds in
74 tomato fruits in field. Studying the deposition, uptake, and distribution dynamics of the pesticides in

75 crop-environment system using dynamiCROP can be helpful to clarify the black box of
76 pesticide-plant-environment system and reduce human exposure to the residue of famoxadone and
77 oxathiapiprolin in tomatoes.

78 In this study, we defined four main goals. First, we develop an analysis method for oxathiapiprolin,
79 IN-E8S72, IN-WR791, and famoxadone in tomatoes and soil based on modified QuEChERS method
80 and high performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). Second, we
81 study the dissipation behavior of famoxadone and oxathiapiprolin in tomato fields and fit the residual
82 pesticide concentration curves with various dissipation kinetic models thereby finding the suitable one
83 for different combinations of pesticide-crop or environment-crop and corresponding half-lives. Third,
84 we use dynamiCROP to simulate the pesticide dynamics in the tomato-environment systems and
85 explain the uptake and translocation processes of famoxadone and oxathiapiprolin over time. Finally,
86 we compare the results of experimental data with dynamiCROP simulation results and estimate the
87 residue fraction in the harvested products and the fraction consumed by humans.

88

89 MATERIALS AND METHODS

90 **Field Trials.** The field experiments that included the dissipation and residue experiments were
91 conducted in Beijing City in the years 2015 and 2016. The experiment date and weather conditions are
92 shown in the Supporting Information, SI (Table S1). With respect to pesticide dissipation in tomato,
93 there was one test treatment and one control treatment. The test treatment consisted of three parallel
94 plots, and each plot was 30 m². No pesticide was sprayed in the control treatment during the whole
95 period of tomato growth.

96 The suspoemulsion of 330 g/L famoxadone and oxathiapiprolin was dissolved in water and

97 sprayed at active constituent level of 165 g a.i./ha (gram of active gradient per hectare, the
98 recommended dosage). About 2 kg tomato samples and 1 kg soil samples were collected at random
99 from several points in each plot at 2 h and 1, 2, 3, 5, 7, 10, 14, 21, 30 (only soil) and 45 (only soil) days
100 after pesticide application. The collected samples of tomato were homogenized with a blender (Philips,
101 China). All samples were stored in a deep freezer at below -18°C until analysis.

102 **Data Analysis.** Most of the considered studies reported that dissipation trends of pesticides in
103 plants fit to pseudo-first-order kinetics, e.g. Zhang et al.,²⁹ according to the following general equation:

104
$$C(t) = C_0 \times e^{-kt} \quad (1)$$

105 where $C(t)$ is the pesticide residue concentration (mg/kg) at the time t (days) between pesticide
106 application and harvest of tomatoes, C_0 is the initial concentration (mg/kg) during pesticide
107 application time and k represents the constant dissipation rate coefficient (day^{-1}).

108 The corresponding half-life ($t_{1/2}$) of pesticides was calculated by using the following equation:

109
$$t_{1/2} = (\ln 2)/k \quad (2)$$

110 However, the dissipation process of pesticides in plants does not only include degradation, but
111 also growth dilution and volatilization.²⁴ Meanwhile, there is also uptake of pesticides from soil
112 into plants which will lead to a negative dissipation in the crops in particular for polar compounds
113 low octanol-water partition coefficient (K_{ow}).³⁰ The variability of dissipation kinetic or half-lives
114 involves many factors, such as pesticides, plant species, sampled plant components (leaves, fruit,
115 straw, etc.) or tissues (nectar, cuticular waxes) and environment (temperature, light/shade
116 conditions, precipitation, etc.).³¹ Thus, it is not accurate that all pesticide-plant-environment
117 combinations were fitted to first-order kinetics. Fantke and Juraske³¹ provide an overview of
118 different dissipation kinetics of various pesticides in a multitude of plant species. Besides that,

119 they summarized different models to fit residual pesticide concentration curves and corresponding
120 dissipation half-lives in plants.

121 In the present study, we fitted the measured residual concentration data of famoxadone and
122 oxathioprolin in tomatoes and soil at different points in time after application to zero-order, half-order,
123 first-order, one-and-a-half-order, second-order, root function first-order, root function
124 one-and-a-half-order, root function second-order kinetics and combined first-first-order as mentioned
125 by Fantke and Juraske.³¹ The most suitable model was identified for calculating half-life according to
126 the fitting results.

127 **Model data collection.** In the model of dynamiCROP, which was a typical mass balance model,
128 residual concentration of a chemical is the net result of competing uptake and elimination process.
129 Plants uptake processes are direct application on to the plant, gaseous and dry/wet particle deposition
130 from air onto cuticles, advective root and foliar uptake. Elimination of chemicals from plants includes
131 volatilization, wash-off, plant growth (biodilution), and microbiological, photolysis, chemical and
132 photodecomposition, metabolism due to oxidation and hydroxylation.^{31,32} To quantify these processes,
133 multiple parameters are required as input for the models including substance properties, plant
134 characteristics, and environmental conditions. Fantke et al.³³ gave an overview about the relevant,
135 essential, and recommended parameters for developing and improving plant accumulation models.
136 Based on his reports, we researched the input data that our model relied on.

137 **Substance -specific input data.** Most frequently reported substance properties to be relevant for
138 pesticide dissipation modeling are partition coefficients K_{ow} , air-water partition coefficient (K_{aw}) and
139 half-lives in plants and soil along with molar mass and application mass. K_{ow} is a key parameter for
140 the root uptake and subsequently translocation in xylem. The polar contaminants (low K_{ow}) are readily

141 soluble in soil pore water, taken up by roots and translocated to stems, leaves and fruits.³⁰ For the
142 leaves role in plant physiology, they have a very high exchange with air, and the volatile contaminants
143 (high K_{aw}) will escape from leaves into air, which demonstrates the significance of K_{aw} for
144 calculation of the accumulation in leaves. The degradation or total dissipation rate is a key variable and
145 half-life ($t_{1/2}$) as an intuitive input parameter is relevant to dissipation kinetic or degradation rate
146 coefficient (k). In our study, the half-lives of famoxadone and oxathiapiprolin in tomatoes ($n=10$) and
147 soil ($n=12$) were derived from dissipation data obtained in the field study, which are shown in the SI
148 (Section S4). Besides that, some other parameters (e.g. substance CAS number, IUPAC name, treat
149 plant components, application rate and formulation) recommended by Fantke et al.³³ to be applied in
150 future testing study and kinetic models were also presented in the SI (Table S2). These data have been
151 identified being of high relevance for developing plant bioaccumulation models.

152 **Crop-specific input data.** Tomato fruit-specific input parameters mainly related to plant lipid,
153 water contents, growth rates, and transpiration stream. Plant lipid or water contents directly impact the
154 transportation, partition and accumulation of polar or non-polar substances in different components.
155 The plants with height above 40 cm are rarely affected by soil particle attachment through rain
156 splashing,³⁴ which was as a major transfer pathway for most persistent lipophilic contaminants to
157 leaves.³⁵ Therefore, plant height or growth rate is an important parameter for crop-specific input data.
158 In our field experiment, the height of the tomato plants when pesticides were sprayed was about 1.3
159 meters. For polar contaminants, which are rapidly translocated from the bottom up, the transpiration
160 rate is among the most important parameters, since the accumulation in leaves is most directly
161 dependent on the transpiration, which was also demonstrated by Trapp and Pussemier.³⁶ In this study,
162 data for the crop-specific parameters for tomatoes simulation were taken from the studies of Fantke et

163 al.²¹ Additional parameters are required to properly define plant species and sampled plant components
164 or tissues (e.g. leaves, fruits or straw).³¹ For example, in our experiment, the scientific crop name is
165 *Lycopersicon esculentum* Mill., and the sampled matrix is tomato fruits, where residues were sampled
166 from the whole fruit.

167 **Environment-specific input data.** Air temperature, vapor pressure, precipitation, soil pH, soil
168 organic carbon (OC) and cation exchange capacity (CEC) are most relevant parameters for kinetic
169 dissipation modeling along with the time between substance application and plant harvest. High
170 temperature and vapor pressure stimulate plant physiological processes such as growth, transpiration
171 and metabolism.^{37,38} Precipitation affects soil particle attachment on leaf surface, because soil particles
172 would attach to the leaves especially when they are located close to the soil surface after rain.³⁰
173 Different amounts of organic carbon in the soil can cause different degrees of adsorption of neutral
174 compounds, thus affecting the distribution of neutral substances in soil and plant roots.³⁹ While for the
175 ionizable organic chemicals, some reports suggests that cation exchange capacity (CEC) of soil is a key
176 determinant for the sorption of cations and soil organic carbon and soil pH are the critical factors for
177 the sorption of anionic chemicals.^{40,41} Beyond that, extreme pH (high or low), will lead to reduced
178 growth, and this may be accompanied by reduced uptake of contaminants.³⁰ These parameters (SI,
179 Table S1) were all recommended to be applied in future testing study and kinetic models.³³

180

181 **RESULTS AND DISCUSSION**

182 **Measured Residues of Famoxadone and Oxathiapiprolin in Tomatoes.** The concentration of
183 famoxadone and oxathiapiprolin, including IN-E8S72 and IN-WR791, were measured using the
184 QuEChERS method and detected by HPLC-MS/MS. Sample pretreatment, HPLC-MS/MS conditions

185 and experimental method validation are shown in the SI, Sections S1-S2. Figure 1 shows the different
186 dissipation kinetic models of famoxadone and oxathiapiprolin in tomato samples in the years 2015 and
187 2016, respectively. The corresponding residual concentration curves and determination coefficient (R^2)
188 are showed in the SI (Table S3). According to the results, the most suitable model for two fungicides in
189 2015 and 2016 was first-order kinetic and second-order kinetic, respectively. For a pesticide, the
190 difference of dissipation trend in two years may be caused by different climatic conditions and crop
191 growth states, which also verified the conclusion of Fantke and Juraske.³¹

192 The half-lives of famoxadone and oxathiapiprolin estimated by the second-order kinetic model
193 (best fit) are 5.2 and 3.0 days in 2016, while the ones obtained from the first-order kinetic model are
194 7.3 and 4.7 days, respectively. It is worth noting that half-lives derived from the best-fit model were
195 lower than obtained using the first-order model. These results are supported by other studies, e.g.
196 Martinez et al.⁴² Compared with first-order kinetics, the second-order model shows the slower
197 diminution of residue throughout the entire dissipation process, as can be observed in Figure 1. Besides,
198 the rate of dissipation is assumed to remain constant in the first-order model, rendering the half-life
199 independent of initial pesticide concentrations. However, in the second-order model, degradation rate
200 and half-life are related to the initial concentrations, with the half-life changing over time.

201 The initial concentrations of famoxadone in tomatoes were 0.2135 and 0.1820 mg/kg in 2015 and
202 2016, respectively. The initial concentrations between the two years were different, which may be
203 caused by the different planting densities or uneven spraying in different years. The half-lives during
204 the two years were 3.4 and 5.2 days, respectively, as calculated according to Table S3 (SI). The reason
205 for different half-lives in two years may be that the precipitation of 2016 is slightly less than 2015.
206 Angioni et al.⁴³ determined the residue concentration of famoxadone in greenhouse tomatoes

207 (Lycopersicon esculentum Mill. cv. Shiran & Caramba) over time with half-life 8.3 days, which is
208 longer than our experimental half-life. Except the difference of plant varieties and field locations, the
209 primary reason for that may be less light exposure and precipitation in greenhouse. The half-lives of
210 famoxadone in other matrix, e.g. grape,^{44,45} spinach⁴⁶ and watermelon leaves⁴⁷ at different conditions
211 (in or on matrix, in field or greenhouse) were also reported, the mean half-lives were 6.3-12.3d. The
212 comparative results showed that the half-lives in fruit crops (18 days in grapes in field or 8.3 day in
213 tomatoes in greenhouse) were longer than leaf crops (6.3 days in spinach and 9.7 days in watermelon
214 leaves in field or 7.7 day in spinach in greenhouse), in crops (18 days in grapes in field) longer than on
215 crops (12.3 days on grapes in field) and in greenhouse (7.7 days in spinach in greenhouse) longer than
216 in field (6.3 days in spinach in field). Pesticides are more easily washed off by rain and loss to air
217 through stomata in leaves, so they dissipate more quickly in leaves than in fruits. Besides, the
218 compounds on the surface of fruit are not only easily washed off by rain, but also may be decomposed
219 by photolysis and photo-decomposition, which results in faster degradation of the pesticide on the crop
220 surface.

221 For oxathiapiprolin, the initial concentrations in our experiments were 0.0290 and 0.0178 mg/kg
222 in 2015 and 2016, with the half-lives 2.4 and 3.0 days, respectively. Consistent with famoxadone, the
223 half-life of 2016 was also longer than that of 2015. While for difference, the dissipation of
224 oxathiapiprolin is quicker than famoxadone in the same condition, which was determined by substance
225 properties. The polarity of oxathiapiprolin is stronger than famoxadone maybe caused that the former
226 was washed off from leaf surface or fruit surface. There were no reports of oxathiapiprolin in other
227 matrix and thus our experiment maybe provides some degradation information of it.

228 **Modeled Residues of Famoxadone and Oxathiapiprolin in Tomatoes.** The model of

229 dynamiCROP was used in this work to study the mass evolution of famoxadone and oxathiapiprolin in
230 eight main compartments [air, soil, leaf deposit (the droplet layer on the leaf surface), fruit deposit
231 (droplet layer on the fruit surface), leaf (leaf interior), fruit (fruit interior), stem, and root] of the tomato
232 environment system. There are three parts that showed mass evolution, which was also explained by
233 Pang et al.⁷ Firstly, the diffusion and transfer of pesticides happened during the initial period. Then
234 during the middle period, the pesticide residues reached maximum levels and subsequently decreased
235 exponentially. In the last part, the pesticide residues degraded for the longest time.

236 Substance properties, plant characteristics, and environmental conditions are three main factors
237 that influenced the dissipation of pesticide residues in plants. The first two factors were stable based on
238 one certain pesticide and plant and could be determined by models. However, the environmental
239 conditions were relatively complex and changeable, which became the limiting factor for modeling,
240 including with dynamiCROP. Among the various environmental conditions, temperature⁴⁸ and
241 precipitation⁷ were considered as the main factors influencing pesticide dissipation trends or half-lives
242 for dynamiCROP. In our work, the average temperature and precipitation during the periods of planting
243 in 2015 and 2016 was not much different (see SI, Table S1). Table S2 (SI) shows the data for $t_{1/2}$
244 tomatoes and $t_{1/2}$ for soil, where the crop degradation rate coefficient and soil degradation rate
245 coefficient are two influential input parameters for the model, which was evaluated by Fantke et al.⁸
246 Their study showed that the crop degradation rate is one of the 10 input parameters, for which model
247 output varies the most across pesticides and crops. In contrast, soil degradation was shown to be a
248 driving parameter only for root and tuber crops (e.g. potato), but not for other crops. This is consistent
249 with our results, where the influence of soil degradation is of minor influence for model output for
250 tomato. Based on that finding, we chose the result of one year (2015) for further analysis.

251 Figure 2 shows the modeled mass evolution of famoxadone and oxathiapiprolin in tomato.
252 Compared with Figure 1, Figure 2 shows that mass evolution of famoxadone and oxathiapiprolin was
253 more complex in the fruit ecosystem. For tomato fruit, there was not only mass exponential decrease,
254 but also the rapid decrease in fruit surface deposits and subsequent increase in fruit interior. During the
255 initial term, famoxadone entered quickly into the air, soil, leaf surface, fruit surface, leaf, and fruit, and
256 then degraded rapidly in the air, leaf surface, and fruit surface. In the air, leaf surface and fruit surface
257 compartments, the residue residence time was less than 1 d (see Table 1). Famoxadone started to appear
258 in root and stem parts in 0.1 d and 3 d, respectively. While for oxathiapiprolin, the pesticide only
259 reached at the air, soil, leaf surface, and fruit surface during the initial term. Thereafter, its mass quickly
260 decreased in the air and leaf surface with the residence time of 0.0099 d and 0.172 d, respectively. To
261 the contrary, in compartments of leaf, fruit, root, and stem, the mass of the pesticide gradually
262 increased. These results showed that pesticides quickly transferred between different compartments
263 after application and the transfer routes were vary depended on different pesticides properties. During
264 the middle period, pesticide mass in leaf, fruit, stem, and root compartments reached maximum values.
265 For famoxadone, maximum mass ranged from 8.5×10^{-6} kg/m² in leaf after 0.3 d to 2.1×10^{-7} kg/m² in
266 stem after 17 d. For oxathiapiprolin, the maximum mass ranged from 7.5×10^{-7} kg/m² in leaf after 1 d
267 to 2.9×10^{-8} kg/m² in root after 3 d. Then the mass of the pesticide decreased exponentially until
268 harvest. There were various reasons for the decrease of pesticide residue, we have explained above.
269 When finally looking at the long-term system behaviors in Figure 2, we realized that the mass of
270 pesticides in all compartments continued to decrease, and the overall system dynamics is driven by a
271 single compartment with the highest residual mass, namely both leaf for famoxadone and
272 oxathiapiprolin, which corresponds to the longest overall residence time in Table 1.

273 **Comparison of Measured and Modeled Residues.** Pesticide residue concentration in tomatoes
274 determined by our developed QuEChERS LC-MS/MS method and the corresponding estimates
275 calculated with the dynamiCROP model are presented in Figure 3. Residues at different points in time
276 after pesticide application were obtained by means of a mass balance system of coupled differential
277 equations that are structured in a matrix system and solved by matrix decomposition. For further details,
278 we refer to Fantke et al.³¹

279 To study the evolution of famoxadone and oxathiapiprolin in tomatoes, modeled and measured
280 residues were compared at time $t=0, 1, 2, 3, 5, 7, 10, 14$ and 21 days after application. The coefficient
281 of determination (R^2) and the standard error (SE) values were the two significant parameters used to
282 evaluate the accuracy of the model. The coefficients of determination for famoxadone were 0.8602 in
283 2015 and 0.8216 in 2016, while for oxathiapiprolin the coefficients of determination were 0.9221 in
284 2015 and 0.8072 in 2016. The SE, which was the standard deviation of the log of residuals between
285 measured and modeled concentrations, was 0.25 for famoxadone in 2015 and 0.27 in 2016, and 0.15
286 for oxathiapiprolin in 2015 and 0.14 in 2016. The R^2 (0.8072-0.9221) and SE (0.14-0.27) indicate that
287 the modeled and measured residue concentrations fitted well. The deviation ranged from 0.0033 for
288 oxathiapiprolin in 2016 to 0.121 for famoxadone in 2015. The deviation between modeled and
289 measured residues for both famoxadone and oxathiapiprolin in 2015 was relatively large, which may be
290 caused by other unconsidered weather conditions (e.g. air humidity or sunlight intensity).

291 **Harvest Fractions and Human Intake Fractions.** Harvest fraction (hF) and intake fraction (iF)
292 are usually used to determine pesticide residue intake by humans via consumption of food crops. The
293 modeled harvest fractions, meaning the fractions of sprayed pesticide masses detected in the harvested
294 fruits, were $7.4 \text{ g}_{\text{in harvest}} \text{ kg}_{\text{applied}}^{-1}$ for famoxadone and $7.8 \text{ g}_{\text{in harvest}} \text{ kg}_{\text{applied}}^{-1}$ for oxathiapiprolin. The

295 physico-chemical properties and the applied quantities were the two factors used for modeling the
296 evolution of pesticide residues.⁹ However, for the low final concentrations of the residues of the two
297 pesticides, there was no much difference between the harvest fractions of famoxadone and
298 oxathiapiprolin.

299 Modeled intake fractions, i.e., the fractions of applied pesticide masses that are potentially
300 ingested through crop consumption, were $3.5 \times 10^{-3} \text{ kg}_{\text{intake}} \text{ kg}_{\text{applied}}^{-1}$ for famoxadone and 3.7×10^{-3}
301 $\text{kg}_{\text{intake}} \text{ kg}_{\text{applied}}^{-1}$ for oxathiapiprolin, which were accounted for by the food processing factor of 0.47 for
302 washing. Variability in intake fractions mainly depended on residue degradation in crops, apart from
303 food processing. For tomato, human intake fractions across pesticides usually vary between 1
304 $\mu\text{g}_{\text{intake}}/\text{kg}_{\text{applied}}$ and $10 \text{ g}_{\text{intake}}/\text{kg}_{\text{applied}}$.^{14, 21} Our results fall well within this range.

305

306 **Supporting Information.** Brief statement in nonsentence format listing the contents of the material
307 supplied as Supporting Information.

308

309 **Notes**

310 The authors declare no competing financial interest.

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434 **FIGURE CAPTIONS**

435 **Figure 1.** Different dissipation kinetic models for famoxadone and oxathiapiprolin during the
436 years of 2015 and 2016 in tomato samples in Beijing, respectively (The most suitable model was
437 expressed with solid line and others dotted lines)

438 **Figure 2.** The modeled mass evolution of famoxadone and oxathiapiprolin in eight main
439 compartments of the tomato ecosystem

440 **Figure 3.** Modeled versus measured residue concentrations (mg/kg) of famoxadone and
441 oxathiapiprolin in tomatoes at time $t=0, 1, 2, 3, 5, 7, 10, 14$ and 21d after the pesticide application
442 in 2015 and 2016

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445 **TABLES**446 **Table 1. Modeled parameters of famoxadone and oxathiapiprolin in tomato**

Parameters		famoxadone	oxathiapiprolin
Residence Times in Compartments (day)	air	0.203	0.099
	soil	13.287	7.242
	Leafsurf.	0.079	0.172
	Fruitsurf.	0.094	4.115
	leaf	13.579	8.132
	fruit	13.573	4.468
	stem	8.659	3.144
	root	5.733	1.256
	Time of maximum mass (day)	$T_{\max, \text{leaf}}$	0.3
$T_{\max, \text{fruit}}$		0.3	1
$T_{\max, \text{stem}}$		17.0	6
$T_{\max, \text{root}}$		8.0	3
Residue at maximum time (mg/kg)	fruit	0.038	0.015

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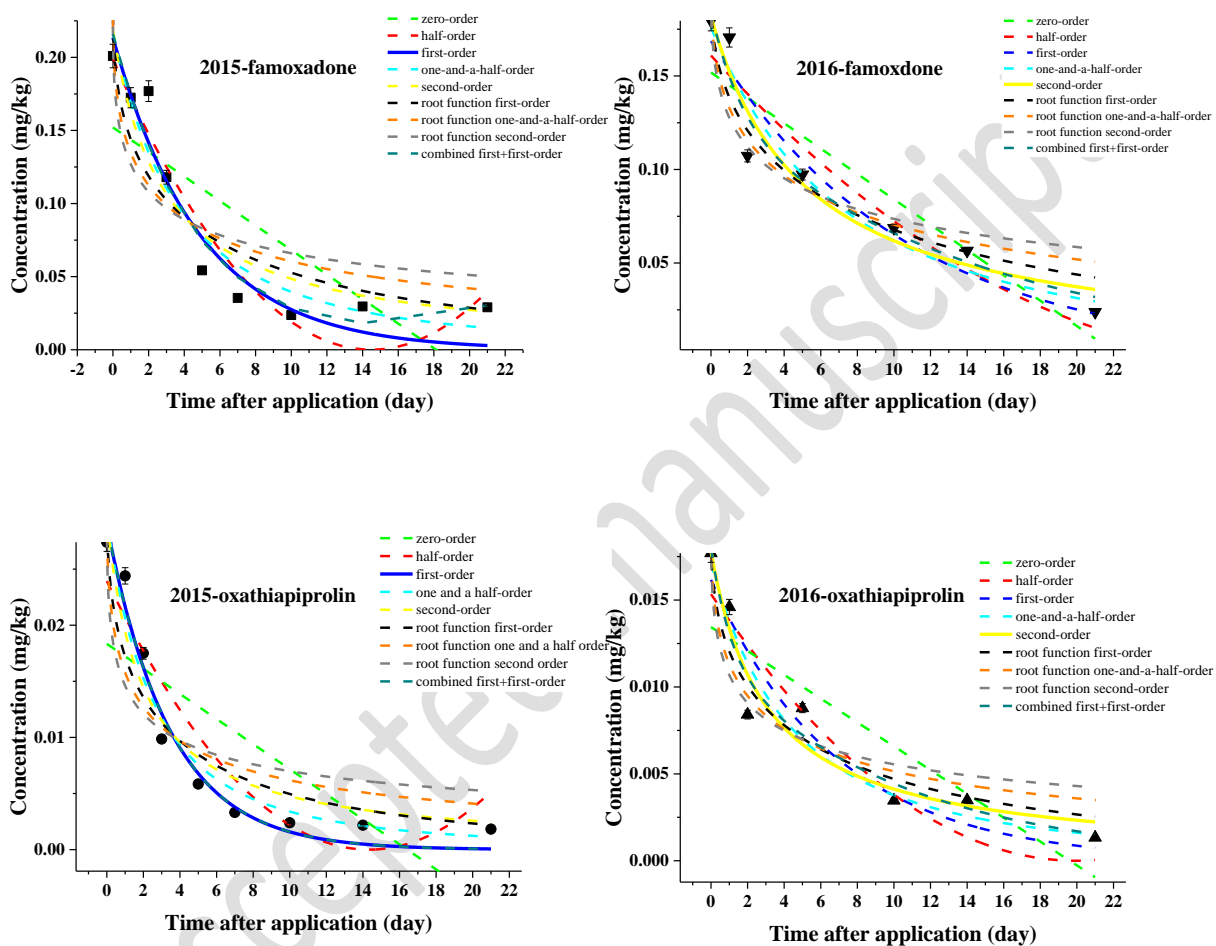
449 **FIGURE GRAPHICS**

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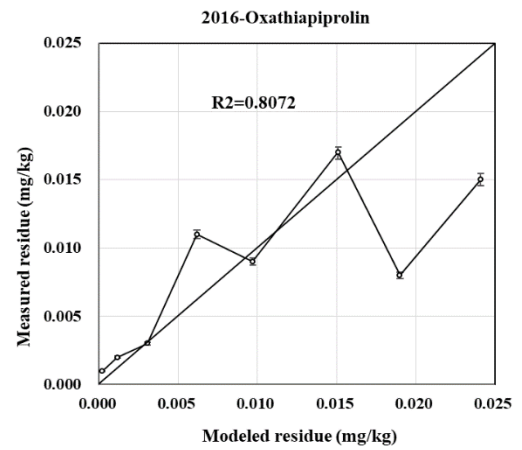
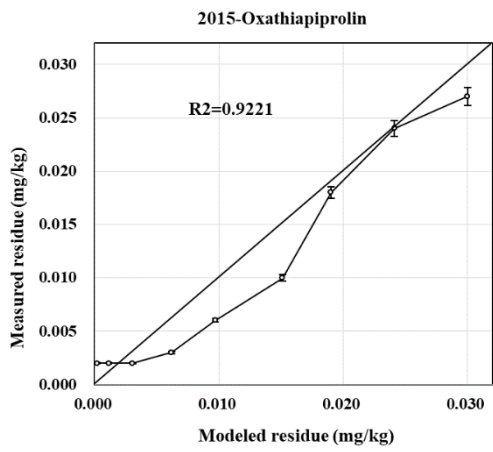
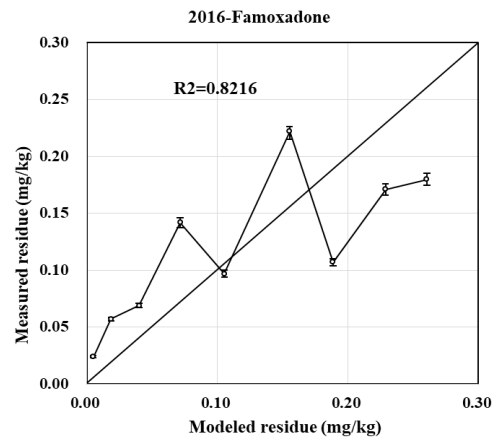
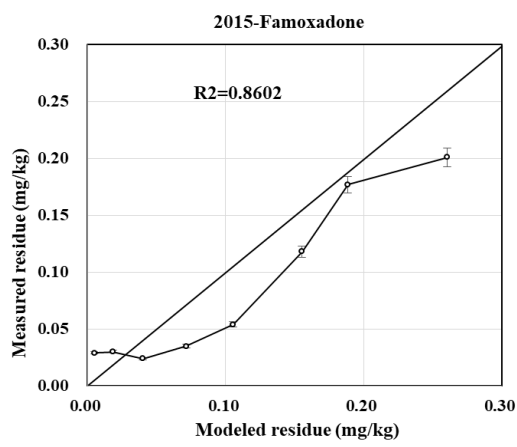
451 **Figure.1**

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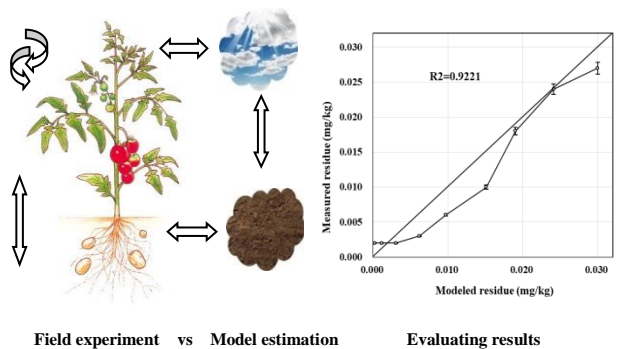
1 **Figure. 3**
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