Supporting Information for

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

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49 **Text S1. Selected Chemicals and Reagents**

50 Standards of oxathiapiprolin (purity was 98.9%), IN-E8S72 (purity was 99.6%), IN-WR791
51 (purity was 99.8%), and famoxadone (purity was 96%) were kindly supplied by Dupont compony
52 (USA). The formulation suspoemulsion (SL), containing 330 g/L famoxadone–oxathiapiprolin, was
53 also provided by Dupont compony (USA). The content of famoxadone was 300 g/L and that of
54 oxathiapiprolin was 30 g/L. HPLC-grade acetonitrile and analytical-grade formic acid (98%) were
55 purchased from Fisher Chemicals (USA) and Sinopharm Chemical Reagent Co. Ltd. (PRC),
56 respectively, while Agela Cleanert C_{18} (Ø 40–60 μm) was purchased from Agela Technologies (Agela,
57 Tianjin, PRC). Sodium chloride (NaCl) and anhydrous magnesium sulfate ($MgSO_4$) were purchased
58 from Beijing Chemical Reagents Company (Beijing, China) and were baked at 110°C for 8 h.

59 **Text S2. Sample Pretreatment.**

60 A sample of 10 g was weighed into a 50 mL plastic centrifuge tube. For tomato samples, 5 mL
61 formic acid water (pH = 3), 10 mL acetonitrile, and 3 g NaCl were then added into the tubes. For soil
62 samples, 5 mL water, 10 mL formic acid acetonitrile (2%, v/v), and 3 g NaCl were added. Thereafter,
63 the samples were vigorously extracted with a vortex mixer for 2 min and centrifuged for 5 min at 3800
64 rpm.

65 A supernatant (1 mL) was transferred into a 2 mL centrifuge tube containing 100 mg anhydrous
66 $MgSO_4$ and 50 mg C_{18}, then mixed for 30 s and centrifuged for 1 min at 10000 rpm. The upper layer
67 (acetonitrile phase) was filtered through a 0.22 μm organic filter membrane and transferred into an auto
68 sampler vial for analysis.

69 **Text S3. HPLC-MS/MS Conditions**

70 All experiments were performed using Agilent Technologies 1200 HPLC series coupled to a

71 triple-quadrupole mass spectrometer (Agilent 6410B Triple Quad) with electrospray ionization (ESI)
72 source. An Athena C18-WP, 100Å column (50 mm × 2.1 mm id, 3.5 μm) was used for separation.
73 Famoxadone and oxathiapiprolin were separated with the mobile phase of methanol and 0.1% formic
74 acid water (v/v = 80/20) and the ions were monitored at positive mode with multiple reaction
75 monitoring (MRM). For the two oxathiapiprolin metabolites, IN-E8S72 and IN-WR791, the mobile
76 phase was acetonitrile and water (v/v = 80/20) and the ESI in negative mode was selected. The flow
77 rate for both processes was 0.3 mL/min and the injection volume was 5 μL, while the column
78 temperature was 30°C and the total run time was 2.5 min.

79 The dry gas (N_2) temperature was 350°C, with the gas flow rate of 8.0 L/min. The nebulizer
80 pressure was 35 psi and the electrospray voltages for both positive and negative modes were 4000 V.
81 Precursor and corresponding product ions for the MRM detection for each target compound are
82 presented in Table S4.

83 **Text S4. Experimental Method Validation**

84 Linearity experiments of famoxadone, oxathiapiprolin, IN-E8S72, and IN-WR791 were
85 performed in the range of 0.005-2 mg/L. Satisfactory linearity was achieved with determination
86 coefficient (R^2) value between 0.9984 and 1.00. The limit of detection (LOD) was the concentration
87 with a signal-to-noise (S/N) ratio of 3, and the limit of quantification (LOQ) was the lowest spiking
88 level. LODs of four compounds ranged from 1.5×10^{-5} mg/kg to 3.8×10^{-5} mg/kg, while LOQs were
89 0.01 mg/kg for famoxadone and 0.02 mg/kg for oxathiapiprolin, IN-E8S72, and IN-WR791, which are
90 presented in Table S5.

91 To evaluate the accuracy and precision of this method, three different concentration levels were
92 spiked into the blank samples with five duplicates. As shown in Table S6, the mean recovery of

93 famoxadone, oxathiapiprolin, IN-E8S72, and IN-WR791 were in the range of 86.0–105.7%, 86.7–
94 108.4%, 79.8–104.3%, and 80.6–103.3%, with the relative standard deviation (RSD) ranging from 1.4%
95 to 4.7%, 1.4% to 4.4%, 1.9% to 5.5%, and 2.9% to 3.6%, respectively. The results were satisfactory
96 according to the residue analysis quality control guide (General Administration of Quarantine of the
97 People's Republic of China, 2002).

98 **Text S5. Measured Residues of Famoxadone and Oxathiapiprolin in Soil**

99 A lot of factors influence the degradation of pesticide in soil, e.g. the pH, water content, content of
100 organic matter, which involves complex chemical and microbial action. In this study, we also used
101 different models to fit the dissipation kinetics of famoxadone and oxathiapiprolin in soil, showed in Fig
102 S1. Table S7 showed the corresponding residual concentration curve and determination coefficient (R^2),
103 from which we can see the most suitable model for famoxadone in 2015 and 2016 both was first-order
104 kinetic. The initial concentrations of famoxadone in soil were 0.1910 and 0.1071 mg/kg with half-lives
105 8.3 day and 6.0 day in 2015 and 2016, respectively. The most suitable model for oxathiapiprolin was
106 seconder-order and root function one-and-a-half-order and the initial concentrations were 0.0082 and
107 0.033 mg/kg with half-lives 11.7 day and 1.2 day in 2015 and 2016, respectively. This part of data is
108 mainly used as model input, and not discussed here.
109

Table S1. Weather and soil condition during the period of tomato planting in the year of 2015 and 2016

		2015	2016
	The date of applied pesticide	6/21/2015	6/9/2016
Weather condition	Precipitation (mm/d)	2.7	2.0
	Average temperature (ºC)	26	25
	Saturated vapor pressure (Pa)	3361	3167.6
Soil condition	pH	6.73	
	Water content (%)	16.64%	
	Content of organic matter (%)	2.3%	
	Cation exchange capacity (cmol/kg)	29.7	

Table S2. Physicochemical properties (MW, molecular weight; Kow, octanol-water partition coefficient; Kaw, air-water partition coefficient; $t_{1/2,tomatoes}$, degradation half-life in tomatoes; t1/2,soil, degradation half-life in soil), substance mass applied in model and experiment, treat plant component, application rate and formulation

Substance	famoxadone	oxathiapiprolin
IUPAC name	(*RS*)-3-anilino-5-methyl-5-(4-phenoxyphenyl)-1,3-oxazolidine-2,4-dione	1-(4-(4-((5*RS*)-5-(2,6-difluorophenyl)-4,5-dihydro-1,2-oxazol-3-yl)-1,3-thiazol-2-yl)-1-piperidyl)-2-(5-methyl-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)ethanone
CAS-RN	131807-57-3	1003318-67-9
MW(g mol^{-1})	374.4	539.52
Log kow	4.65	3.66
Log kaw	-2.34	-2.45
$t_{1/2}$ tomatoes (d)	3.2/5..2	2.4/3.0
$t_{1/2}$ soil (d)	8.3/6.0	11.7/1.2
$m_{applied\ in\ model}$ (g.a.i/ha)	165	
$m_{applied\ in\ experiment}$ (g.a.i/ha)	165	
Treat plant component(s)	Foliar application	
Application rate (kg/m^2/d)	0	
Formulation (%)	90.9	9.1

Table S3. Different models to fit residual pesticide concentration curves and estimate corresponding determination coefficient (R^2) for famoxadone and oxathiapiprolin in tomatoes.

models	famoxadone				oxathiapiprolin			
	2015		2016		2015		2016	
	Residual concentration curve	R^2	Residual concentration curve	R^2	Residual concentration curve	R^2	Residual concentration curve	R^2
Zero-order	$C(t) = 0.1520 - 0.0084t$	0.56975	$C(t) = 0.1518 - 0.0068t$	0.80569	$C(t) = 0.01834 - 0.00112t$	0.53129	$C(t) = 0.0134 - 6.856E - 4t$	0.72331
Half-order	$C(t) = (-0.4457 + 0.0307t)^2$	0.91598	$C(t) = (-0.4012 + 0.0132t)^2$	0.86499	$C(t) = (-0.1547 + 0.0108t)^2$	0.8664	$C(t) = (-0.1239 + 0.0062t)^2$	0.87251
First-order	$C(t) = 0.2135e^{-0.2049t}$	0.91705	$C(t) = 0.1686e^{-0.0951t}$	0.90035	$C(t) = 0.0290e^{-0.2905t}$	0.96564	$C(t) = 0.01626e^{-0.1464t}$	0.89542
One-and-a-half-order	$C(t) = \frac{1}{(2.1442 + 0.2883t)^2}$	0.90494	$C(t) = \frac{1}{(2.3843 + 0.1635t)^2}$	0.93468	$C(t) = \frac{1}{(5.8191 + 1.1355t)^2}$	0.95041	$C(t) = \frac{1}{(7.6404 + 0.8643t)^2}$	0.90494
Second-order	$C(t) = \frac{0.2138}{1 + 0.3513t}$	0.86856	$C(t) = \frac{0.1820}{1 + 0.1939t}$	0.94119	$C(t) = \frac{0.0296}{1 + 0.5240t}$	0.90981	$C(t) = \frac{0.01782}{1 + 0.3320t}$	0.93295
Root function first-order	$C(t) = 0.2290e^{-0.4646\sqrt{t}}$	0.79168	$C(t) = 0.1930e^{-0.3313\sqrt{t}}$	0.89447	$C(t) = 0.0306e^{-0.5751\sqrt{t}}$	0.85045	$C(t) = 0.0186e^{-0.4348\sqrt{t}}$	0.91338
Root function one-and-a-half-order	$C(t) = \frac{1}{(2.1025 + 0.6212\sqrt{t})^2}$	0.72143	$C(t) = \frac{1}{(2.2686 + 0.4738\sqrt{t})^2}$	0.87487	$C(t) = \frac{1}{(5.7614 + 2.1998\sqrt{t})^2}$	0.77584	$C(t) = \frac{1}{(7.3016 + 2.0990\sqrt{t})^2}$	0.86755
Root function second-order	$C(t) = \frac{0.2210}{1 + 0.7431\sqrt{t}}$	0.6534	$C(t) = \frac{0.1934}{1 + 0.5151\sqrt{t}}$	0.79833	$C(t) = \frac{0.0294}{1 + 1.0153\sqrt{t}}$	0.70423	$C(t) = \frac{0.0187}{1 + 0.7469\sqrt{t}}$	0.81375
Combined first+first-order	$C(t) = 0.0055e^{-0.4385t} + 0.0174e^{-0.0544t}$	0.9140	$C(t) = 0.0598e^{-0.0403t} + 0.0602e^{-0.9787t}$	0.8998	--	--	$C(t) = 0.0058e^{-0.0560t} + 0.0006e^{-1.3866t}$	0.9043

Note: "--" represents that the residual concentration curve could not be estimated by corresponding model

Table S4. HPLC-MS/MS parameters of famoxadone, oxathiapiprolin, IN-E8S72 and IN-WR791

Compounds	t_R(min)	HPLC-MS/MS				
		Quantification ion transition	Collision energy (eV)	Confirmatory ion transition	Collision energy (eV)	Fragmentor (eV)
famoxadone		392.2-238.2	10	392.2-195	25	90
				392.2-93.2	40	
oxathiapiprolin		540.1-500.1	25	540.1-350.1	30	140
				540.1-167.1	25	
IN-E8S72		179-135.1	5	179-65.1	15	60
IN-WR791		207.1-143.1	10	207.1-163.1	5	70
				207.1-123.1	15	

Table S5. The calibration curves, coefficient of determination (R^2) and LOD/LOQs of famoxadone, oxathiapiprolin, IN-E8S72 and IN-WR791 in tomatoes and soil

Matrix	Compound	Calibration curve	R^2	LOD (mg/kg)	LOQ (mg/kg)
tomatoes	famoxadone	y = 12,578.94 x + 3.57	1.00	4.2×10^{-5}	0.01
	oxathiapiprolin	y = 78907x - 973.86	0.9984	1.5×10^{-5}	0.02
	IN-E8S72	y = 47,070.05 x - 369.76	0.9984	3.8×10^{-4}	0.02
	IN-WR791	y = 103279x - 1426.3	0.9989	2.2×10^{-4}	0.02
soil	famoxadone	y = 27306x + 810.2	0.9985	8.6×10^{-5}	0.01
	oxathiapiprolin	y = 94508x + 97.356	1.00	1.8×10^{-5}	0.02
	IN-E8S72	y = 27306x + 810.2	0.9985	2.2×10^{-4}	0.02
	IN-WR791	y = 35239x - 49.903	0.9999	2.1×10^{-4}	0.02

Table S6. Recoveries (n=5) and RSD of famoxadone, oxathiapiprolin, IN-E8S72 and IN-WR791 in tomatoes and soil

Matrix	Compound	Fortified level (mg/kg)	Average recovery (%)	RSD (%)
tomatoes	famoxadone	0.01	99.3±3.6	3.1
		0.02	105.7±5.5	4.7
		0.1	97.7±2.4	2.1
	oxathiapiprolin	0.02	100.4±2.4	2.1
		0.2	108.4±4.3	4.4
		0.5	100.2±2.6	2.3
	IN-E8S72	0.02	101.5±1.5	1.9
		0.2	101.5±1.5	5.0
		0.5	104.3±2.3	3.1
	IN-WR791	0.02	80.6±3.4	3.6
		0.2	103.3±2.6	3.1
		0.5	99.0±3.2	3.2
soil	famoxadone	0.01	87.0±1.2	1.4
		0.02	86.0±1.7	1.9
		0.1	95.0±2.9	3.1
	oxathiapiprolin	0.02	93.0±2.2	2.3
		0.2	86.7±1.2	1.4
		0.5	93.3±3.2	3.5
	IN-E8S72	0.02	97.6±2.8	2.8
		0.2	79.8±2.8	3.5
		0.5	80.2±3.8	4.8
	IN-WR791	0.02	88.4±2.6	2.9
		0.2	88.1±2.9	3.3
		0.5	81.0±2.8	3.5

Table S7. Different models to fit residual pesticide concentration curves and estimate corresponding determination coefficient (R^2) for famoxadone and oxathiapiprolin in soil.

models	famoxadone				oxathiapiprolin			
	2015		2016		2015		2016	
	Residual concentration curve	R^2	Residual concentration curve	R^2	Residual concentration curve	R^2	Residual concentration curve	R^2
Zero-order	$C(t) = 0.0759 - 0.0016t$	0.9096	$C(t) = 0.0843 - 0.0022t$	0.6042	$C(t) = 0.0634 - 1.3570\ E - 4t$	0..6136	$C(t) = 0.0108 - 2.949E - 4t$	0.5691
Half-order	$C(t) = (-0.3240 + 0.0057t)^2$	0.9646	$C(t) = (-0.3129 + 0.0013t)^2$	0.8782	$C(t) = (-0.0859 + 0.0017t)^2$	0.7920	$C(t) = (-0.1080 + 0.0019t)^2$	0.6197
First-order	$C(t) = 0.1910e^{-0.0833t}$	0.9796	$C(t) = 0.1071e^{-0.1147t}$	0.9096	$C(t) = 0.0077e^{-0.0501t}$	0.8730	$C(t) = 0.0132e^{-0.0499t}$	0.6877
One-and-a-half-order	$C(t) = \frac{1}{(1.5001 + 0.2766t)^2}$	0.7184	$C(t) = \frac{1}{(3.0241 + 0.2267t)^2}$	0.8944	$C(t) = \frac{1}{(11.2010 + 0.3656t)^2}$	0.9108	$C(t) = \frac{1}{(8.0576 + 0.3196t)^2}$	0.7763
Second-order	$C(t) = \frac{0.0174}{1 + 0.0449t}$	0.4481	$C(t) = \frac{0.1109}{1 + 0.1930t}$	0.8635	$C(t) = \frac{0.0082}{1 + 0.08511t}$	0.9242	$C(t) = \frac{0.0190}{1 + 0.1500t}$	0.8709
Root function first-order	$C(t) = 0.7120e^{-0.7444\sqrt{t}}$	0.8309	$C(t) = 0.1190e^{-0.3370\sqrt{t}}$	0.7956	--	--	--	--
Root function one-and-a-half-order	$C(t) = \frac{1}{(0.6562 + 0.2695\sqrt{t})^2}$	0.3524	$C(t) = \frac{1}{(2.9034 + 0.6052\sqrt{t})^2}$	0.7249	$C(t) = \frac{1}{(9.6347 + 1.7708\sqrt{t})^2}$	0.9148	$C(t) = \frac{1}{(5.4654 + 2.0296\sqrt{t})^2}$	0.9040
Root function second-order	$C(t) = \frac{0.5836}{1 + 29.0220\sqrt{t}}$	0.0466	$C(t) = \frac{0.1171}{1 + 4.3091\sqrt{t}}$	0.6546	$C(t) = \frac{0.0016}{1 + 5.8023\sqrt{t}}$	0.9015	$C(t) = \frac{0.0221}{1 + 2.8118\sqrt{t}}$	0.7986
Combined first+first-order	--	--	--	--	$C(t) = 0.0035e^{-0.0357t} + 0.0032e^{-0.0741t}$	0.9153	$C(t) = 0.0118e^{-0.6517t} + 0.0059e^{-0.2771t}$	0.9030

Note: "--" represents that the residual concentration curve could not be estimated by corresponding model

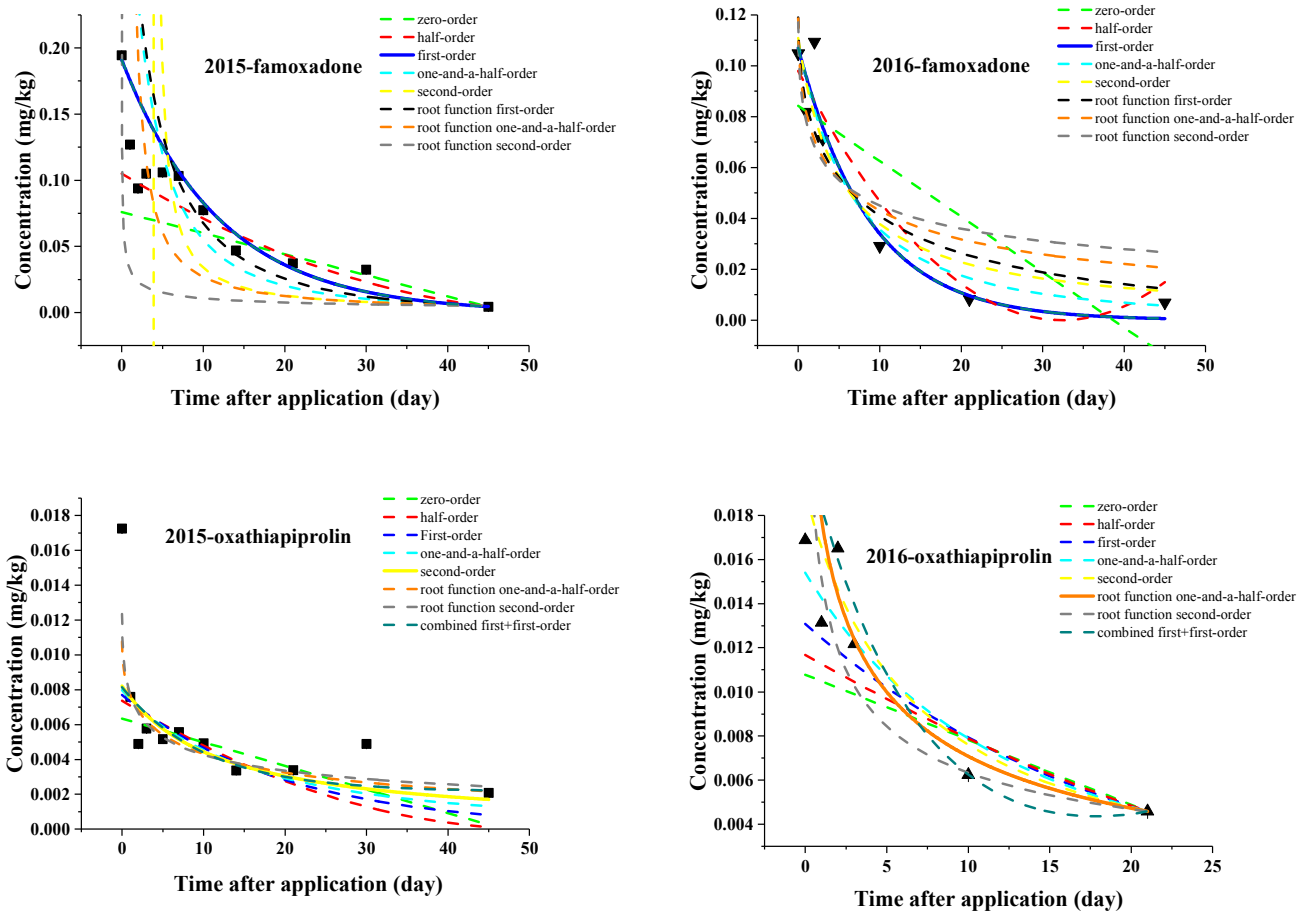

Figure S1. Different dissipation kinetic models for famoxadone and oxathiapiprolin during the years of 2015 and 2016 in soil samples in Beijing, respectively (The most suitable model was expressed with solid line and others dotted lines)