Simultaneous determination of thiacloprid and its five metabolites in vegetables and flowers via QuEChERS combined with HPLC-MS/MS

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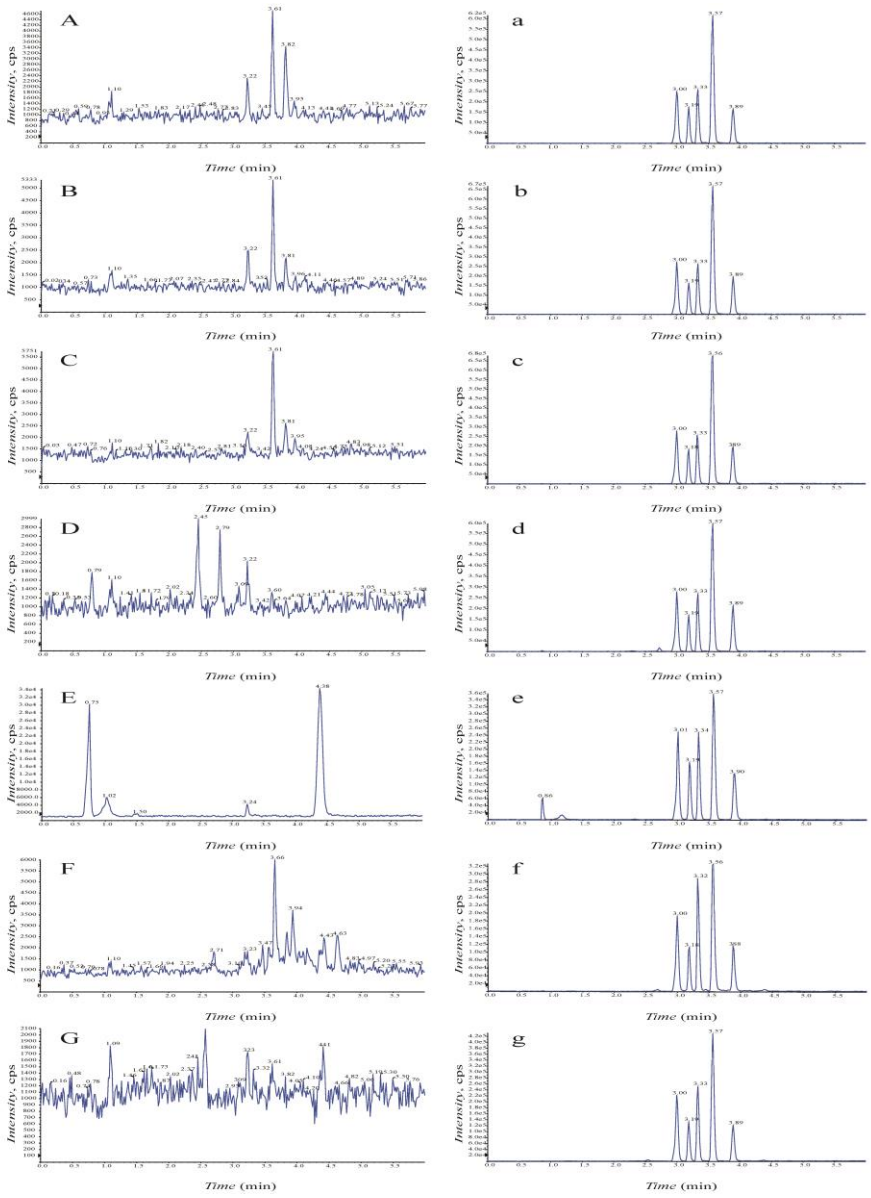

Fig. S1. Typical HPLC-MS/MS MRM chromatograms of thiacloprid and its six metabolites of (A) blank cowpea sample, (B) blank cucumber sample, (C) blank muskmelon sample, (D) blank tomato sample, (E) blank cotton flower sample, (F) blank chrysanthemum flower sample, (G) blank mixed wildflower sample, (a) spiked cowpea samples (100 μg kg^{-1}), (b) spiked cucumber sample (100 μg kg^{-1}), (c) spiked muskmelon sample (100 μg kg^{-1}), (d) spiked tomato sample (100 μg kg^{-1}), (e) spiked cotton flower sample (100 μg kg^{-1}), (f) spiked chrysanthemum flower sample (100 μg kg^{-1}), (g) spiked mixed wildflower sample (100 μg kg^{-1}).

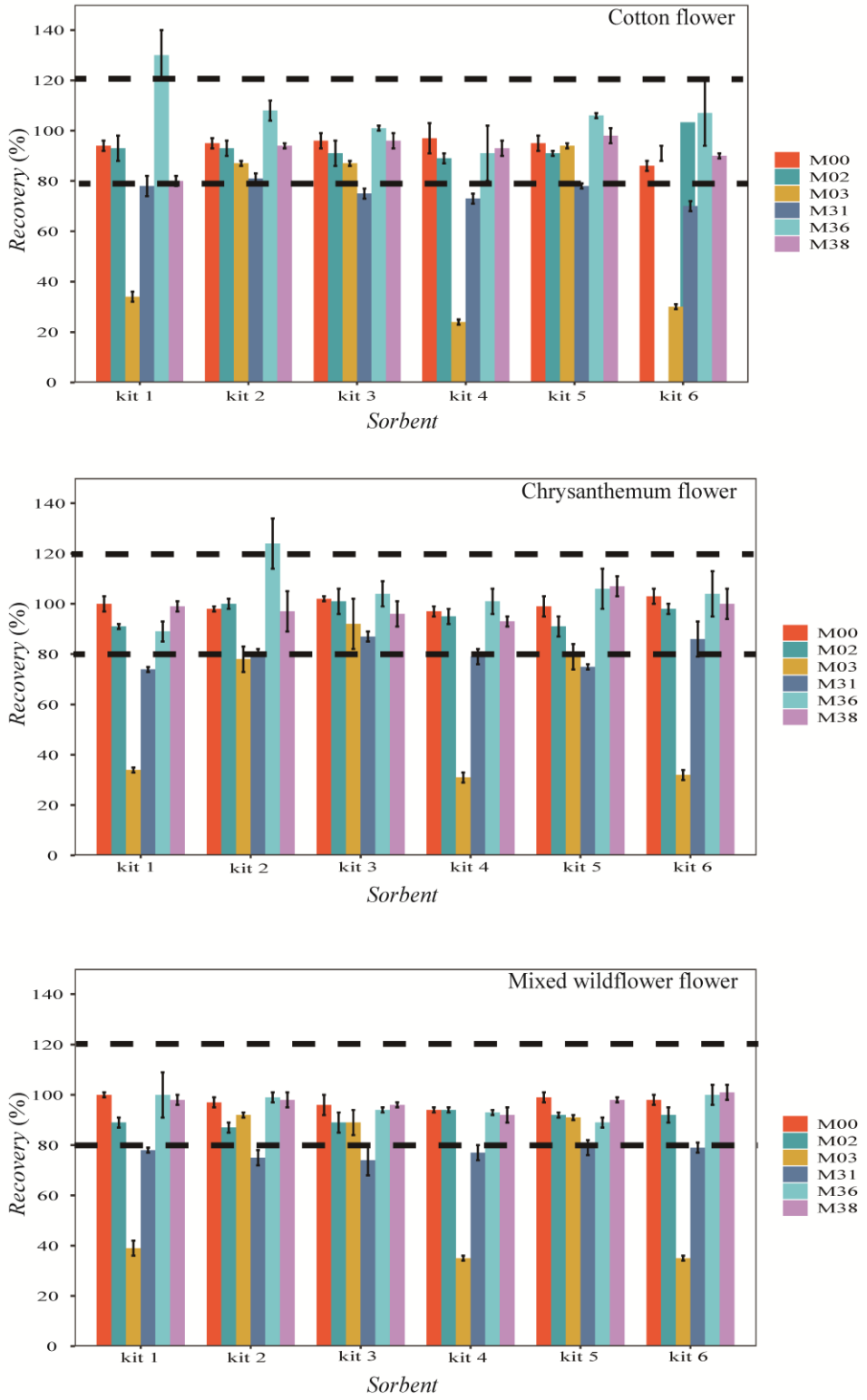

Fig. S2. Effects of six different sorbent kits on extraction recovery of thiacloprid and its five metabolites in different flowers

Table S1. The MS basic instrument parameters setting

	ESI mode	
Instrumental parameters	ESI+	ESI-
ion spray voltage (V)	5500	-4500
ESI source temperature (℃)	500	500
Ion Source Gas 1 (GS 1)	50	50
Ion Source Gas 2 (GS 2)	50	50
Curtain Gas (CUR)	40	40
collision gas (CAD)	9	9
DP	-40	-40
EP	-10	-10
CE	38.0	-15
CXP	6.0	-11

Declustering Potential (DP), Entrance Potential (EP), Collision Cell Exit Potential (CPX), and Collision Energy (CE). All expressed in Volt (V).

Table S2. Calibration curve, linearity, matrix effect and LOQ of thiacloprid and its metabolites

Compound	Matrix	Regression equation	R^2	ME	LOQ
M00	Acetonitrile	y = 5613.15638x + 3677.10769	0.99895	_	_
	cowpea	y = 4672.98788x + 36377.2	0.99935	0.83	2
	cucumber	y = 4860.71864x + 37825.5	0.99753	0.87	2
	muskmelon	y = 5233.85370x + 48319.3	0.99883	0.93	2
	tomato	y = 4892.50419x + 7724.99921	0.99902	0.87	2
	cotton flower	y = 2767.74035x + 3061.67211	0.99965	0.49	2
	chrysanthemum flower	y = 2918.89839x + 2685.13282	0.99998	0.52	2
	mixed flower sample	y = 3372.72101x + 5528.79500	0.99983	0.60	2
M02	Acetonitrile	y = 2620.43615x - 1038.31920	0.99669	_	_
	cowpea	y = 2709.45896x + 3094.92423	0.99895	1.03	2
	cucumber	y = 2626.04274x + 2310.73125	0.99989	1.00	2
	muskmelon	y = 2665.25264x + 1880.85410	0.99993	1.02	2
	tomato	y = 2636.73450x + 2267.78149	0.99977	1.01	2
	cotton flower	y = 2381.46472x + 1605.46503	0.99976	0.91	2
	chrysanthemum flower	y = 2829.76786x + 2167.59524	0.99991	1.08	2
	mixed flower	y = 2588.53848x + 2263.95870	0.99946	0.99	2

	sample				
M03	Acetonitrile	y = 2525.57993x + 5.86330	0.99992	_	_
	cowpea	y = 2936.98705x + 40251.1	0.9986	1.16	2
	cucumber	y = 3013.12483x + 16259.74807	0.99832	1.19	2
	muskmelon	y = 3270.28509x + 28969.67781	0.99882	1.29	2
	tomato	y = 3006.54985x + 6714.58132	0.99949	1.19	2
	cotton flower	y = 2162.13846x + 346752	0.99802	0.86	2
	chrysanthemum flower	y = 2466.09673x + 8119.31849	0.99568	0.98	2
	mixed flower sample	y = 1104.04749x + 2705.83436	0.99998	0.44	2
M31	Acetonitrile	y = 4052.30722x - 908.14449	0.99944	_	_
	cowpea	y = 4115.59092x + 2143.89003	0.99767	1.02	2
	cucumber	y = 3893.04414x + 3573.60829	0.99955	0.96	2
	muskmelon	y = 3993.52346x + 1820.16819	0.99996	0.99	2
	tomato	y = 4064.50745x + 3996.14392	0.9991	1.00	2
	cotton flower	y = 3202.22460x + 4080.79169	0.99997	0.79	2
	chrysanthemum flower	y = 3367.92637x + 2380.51881	0.99972	0.83	2
	mixed flower	y = 3317.10934x + 3855.96736	0.9998	0.82	2

	sample				
M36	Acetonitrile	y = 2518.07115x - 378.84128	0.99883	_	_
	cowpea	y = 2362.82302x + 18016.17213	0.99884	0.82	2
	cucumber	y = 2359.09446x + 16130.43826	0.99837	0.99	2
	muskmelon	y = 2397.23825x + 40465.8	0.99711	1.15	2
	tomato	y = 2448.97453x + 17040.45634	0.9995	0.81	2
	cotton flower	y = 2135.18631x + 35578.3	0.99964	0.97	2
	chrysanthemum flower	y = 1879.95484x+6423.57558	0.99943	0.95	2
	mixed flower sample	y = 2021.37028x + 8946.11665	0.99967	0.78	2
M38	Acetonitrile	y = 4896.17489x + 2630.41867	0.99928	_	_
	cowpea	y = 4015.12258x + 4907.09713	0.99897	0.82	2
	cucumber	y = 4150.65842x + 7673.27139	0.99719	0.85	2
	muskmelon	y = 4578.73116x + 6817.59279	0.9971	0.94	2
	tomato	y = 4344.34306x + 6621.92223	0.99807	0.89	2
	cotton flower	y = 2208.30379x + 1607.18794	0.99925	0.45	2
	chrysanthemum flower	y = 2544.04051x + 2367.41175	0.99979	0.52	2

	mixed flower sample	y = 2730.20975x + 4101.70149	1	0.56	2

Table S3. Average recoveries (n = 15, %), RSD_r (%), and RSD_R (%) for target compounds from different flower matrices at three spiked levers.

Matrix		cotton flower			chrysanthemum flower			mixed wildflower sample		
compounds	Spike level (μg kg-1)	Recovery	intra-RSD	inter-RSD	Recovery	intra-RSD	inter-RSD	Recovery	intra-RSD	inter-RSD
M00	2000	95	6.8	4.8	95	3.8	4.2	100	3.5	7.2
	200	95	5.2	2.8	98	1.8	2.9	100	5.4	8.2
	2	97	10.5	6.5	105	11.0	10.9	93	10.2	4.8
M02	2000	91	2.1	4.1	94	2.6	6.7	96	3.1	3.7
	200	97	2.5	1.1	99	1.5	3.7	90	4.3	1.2
	2	90	4.5	11.8	105	12.0	5.6	102	7.3	7.4
M31	2000	78	3.0	7.1	83	1.6	3.7	85	2.2	6.6
	200	79	6.9	8.8	83	3.0	1.8	80	6.8	7.5
	2	84	5.5	5.9	77	11.8	14.4	81	5.6	5.1
M38	2000	96	3.2	5.4	98	2.4	3.3	102	2.2	8.3
	200	99	5.8	3.8	99	1.6	2.4	100	8.6	9.4
	2	94	9.9	14.1	94	1.0	12.4	94	6.2	12.1
M36	2000	97	3.4	4.0	93	4.5	5.6	100	4.3	4.0
	200	98	4.5	4.2	98	2.3	6.0	95	4.7	4.6
	2	105	11.5	2.9	108	11.7	11.6	119	12.8	9.8
M03	2000	77	5.7	8.9	91	4.2	3.4	88	5.0	10.7
	200	89	13.4	9.1	93	3.6	6.4	94	3.4	7.2
	2	104	4.6	14.0	86	13.1	6.4	97	1.0	3.0

Table S4. The detection result of thiacloprid and its metabolites in flower samples collected from the farm.

Latin name of species (flower samples)	Thiacloprid (μg kg^{-1})	M02 (μg kg^{-1})	M03 (μg kg^{-1})	M31 (μg kg^{-1})	M36 (μg kg^{-1})	M38 (μg kg^{-1})
Polygonum viscosum Buch.-Ham.ex D.Don.	ND	ND	ND	ND	ND	ND
Gerbera jamesonii Bolus	ND	ND	7.3	ND	13.8	ND
Erigeron annuus (Linn.) Pers.	ND	ND	ND	ND	3.3	ND
Punica granatum Linn.	ND	ND	1.8	ND	2.1	ND
Dendranthema indicum (Linn.) Des Moul	ND	ND	ND	ND	ND	ND
Hypericum monogynum Linn.	ND	ND	ND	ND	5.6	ND
Sambucus willimsii Hance	ND	ND	ND	ND	2.1	ND
Hibiscus syriacus Linn.	ND	ND	55.9	ND	3.7	ND
Trifolium repens Linn.	ND	ND	122.4	ND	3.4	ND
Rosa chinensis Jacq.	ND	ND	ND	ND	5.0	ND
Verbena officinalis Linn.	ND	ND	ND	ND	4.8	ND
Daucus carota Linn.	ND	ND	35.1	ND	2.2	ND

Cosmos bipinnata Cav.	ND	ND	4.5	ND	2.6	ND
Campsis grandiflora (Thunb.) Schum.	ND	ND	ND	ND	2.4	ND
Ligustrum lucidum Ait.	ND	ND	ND	ND	2.6	ND
Alternanthera philoxeroides (Mart.) Griseb.	ND	ND	ND	ND	5.2	ND
Helianthus annuus Linn.	ND	ND	ND	ND	ND	ND
Cichorium intybus Linn.	ND	ND	10.6	ND	2.1	ND
Brassica campestris L.	ND	ND	42.5	ND	162.4	ND

All flowers were collected from this farm and their species names are expressed using their Latin names.