

ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Development of a high throughput multi-residue method for analysis of common pesticides in aquatic environment by automated online solid phase extraction coupled to LC-MS/MS

Table of Content

Fig. S1 LC-MS/MS chromatogram of pesticides under online SPE conditions (100 ng/L, DW).

Fig. S2 Relative intensity variations of all pesticides under different loading flowrates.

Fig. S3 Peak area variations with the increasing of injection volume.

Table S1 Mass spectrometry parameters of all pesticides and their corresponding internal standards

Table S2 Information on treatment process and capacity of WWTPs

Table S3 Relative recoveries (%) of each pesticide on the four online SPE cartridges

Table S4 Influence of MeOH contents in loading/wash solvent on the analyte recoveries (% , n=5)

Table S5 Influence of wash volume on the analyte recoveries (%)

Table S6 Influence of loading/wash flowrate on the analyte recoveries (%)

Table S7 Matrix effect (%) of all pesticides in the three matrixes.

Table S8 Matrix spiking recovery (%) of every pesticide in the three matrixes (n=5)

Table S9 Relative deviation of ion ratio of pesticides in spiked DW samples (% , n=5)

Table S10 Relative deviation of ion ratio of pesticides in spiked SW samples (% , n=5)

Table S11 Relative deviation of ion ratio of pesticides in spiked WWE samples (% , n=5)

Table S12 Relative deviation of ion ratio of pesticides in WWE samples (%)

Table S13 Linearity coefficient of each pesticide in the two ranges

Table S14 MDLs and MQLs of each pesticide in the three matrixes

Table S15 Intra-day and inter-day precision of each pesticide

Table S16 Concentration (ng/L) and detection frequency (DF, %) of pesticides in WWE samples of 12 WWTPs

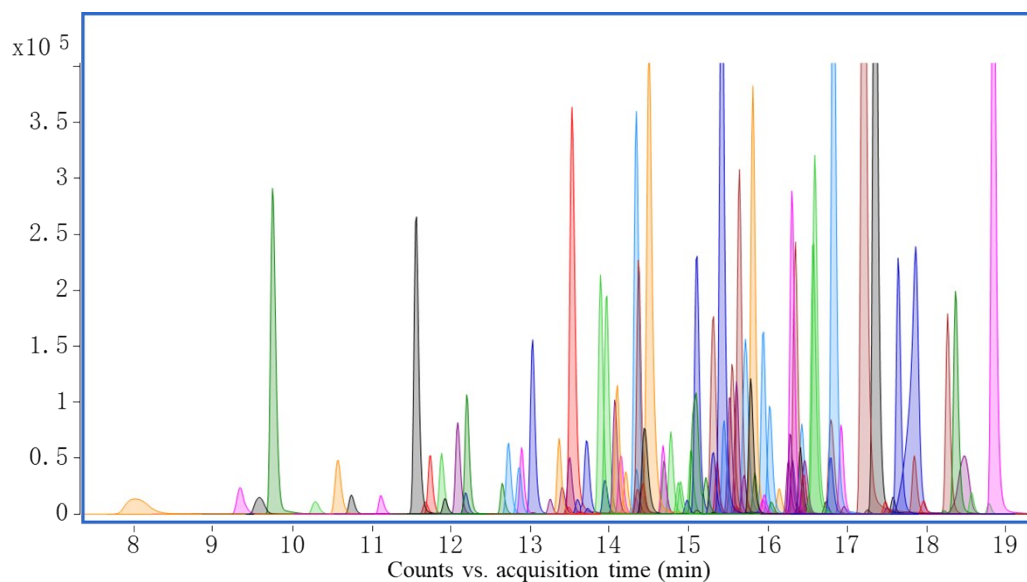


Fig. S1 LC-MS/MS chromatogram of pesticides under online SPE conditions (100 ng/L, DW)

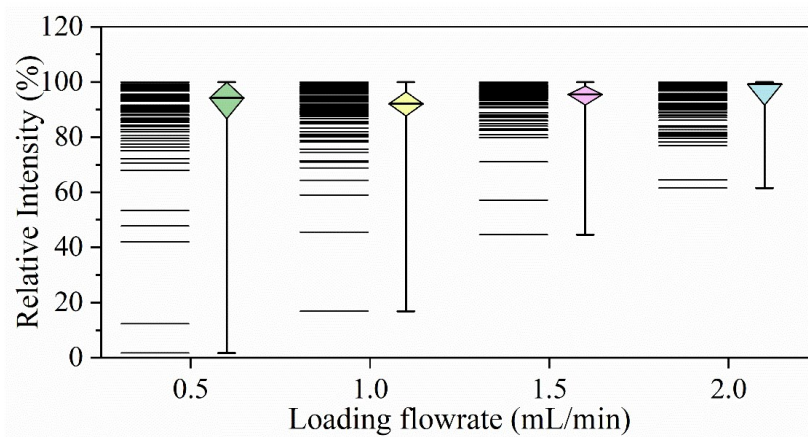


Fig. S2 Relative intensity variations of all pesticides under different loading flowrates

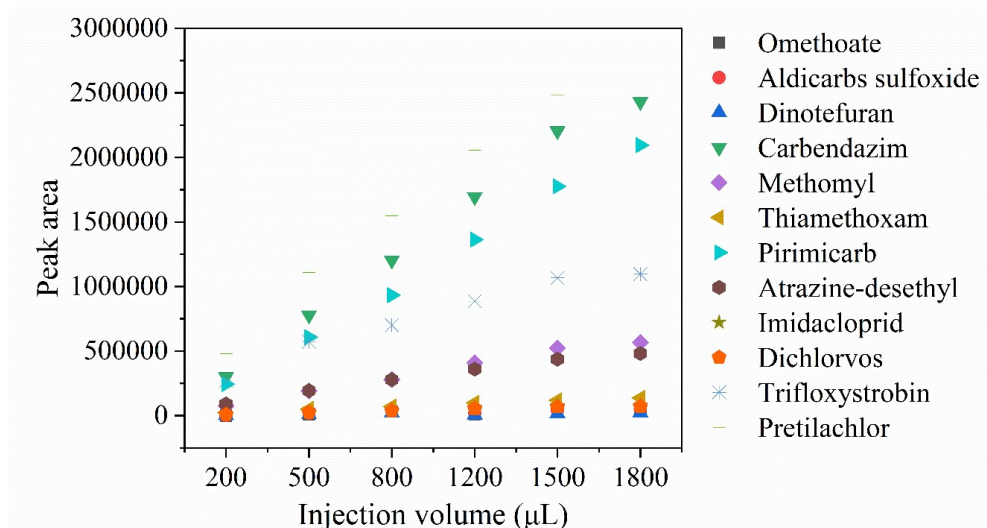


Fig. S3 Peak area variations with the increasing of injection volume

Table S1 Mass spectrometry parameters of all pesticides and their corresponding internal standards

Chemical name	Precursor ion (m/z)	RT (min)	Fragment or (V)	Quantification ion (m/z)/CE (V)	Confirmation ion (m/z)/CE (V)	Polarity	ILISs
Paclobutrazol	294.2	15.1	140	70/20	125/45	Positive	Isoproturon-d6
Acetochlor	270.1	16.4	95	133.1/36	148.1/36	Positive	Acetochlor-d11
Acetochlor-d11	281.6	16.4	85	59.4/16	235.6/8	Positive	–
Alachlor	270.1	16.4	60	238.1/5	147.1/37	Positive	Acetochlor-d11
Butachlor	312.2	18.4	125	238/9	147.1/40	Positive	Acetochlor-d11
Metolachlor	284.8	16.4	110	253.1/13	177.1/29	Positive	Acetochlor-d11
Pretilachlor	312.2	17.8	130	252.1/24	176.1/32	Positive	Acetochlor-d11
Ametryn	228.1	13.5	125	186/21	116/29	Positive	Atrazine-d5
Atrazine	216.1	14.3	110	174/20	133.1/25	Positive	Atrazine-d5
Atrazine-d5	221.2	14.3	150	179.1/20	69.1/44	Positive	–
Atrazine-desethyl	188.1	11.8	150	146.1/17	146.1/17	Positive	Atrazine-desethyl-d7
Atrazine-desethyl-d7	195.1	11.8	129	160/20	132/36	Positive	–
Atrazine-desisopropyl	174	10.7	140	96/21	132/17	Positive	Atrazine-d5
Cyanazine	241.1	13.5	150	214.1/20	205.1/20	Positive	Atrazine-d5
Prometryn	242.2	14.5	155	158.1/28	200.1/20	Positive	Atrazine-d5
Simazine	202.1	13.3	150	132/20	124/20	Positive	Atrazine-d5
Terbutylazine	230.1	15.4	110	174/17	132/29	Positive	Atrazine-d5
Terbutryn	242.1	14.5	110	186/17	71.1/37	Positive	Atrazine-d5
Bensulfuron-methyl	411.1	14.7	115	149/24	182/24	Positive	Isoproturon-d6
Ethametsulfuron-methyl	411.1	14.0	120	196.1/16	170.1/12	Positive	Nicosulfuron-d6
Nicosulfuron	411.1	12.9	105	182/20	213/16	Positive	Nicosulfuron-d6
Nicosulfuron-d6	417.5	12.9	119	188.2/20	213.2/16	Positive	–
Pyrazosulfuron-ethyl	415.2	15.4	115	182.2/20	139.2/45	Positive	Atrazine-d5
Tribenuron-methyl	396.1	14.9	95	155/13	198.9/17	Positive	Isoproturon-d6
Diflufenican	395.3	17.5	140	266/25	246/40	Positive	Atrazine-d5
Diuron	233	14.4	130	72/21	160/33	Positive	Isoproturon-d6
Isoproturon	207.2	14.3	115	165.1/13	134.1/25	Positive	Isoproturon-d6
Isoproturon-d6	213.2	14.3	120	78.1/28	52.2/20	Positive	–
Chlortoluron	213.1	14.0	135	72/25	140/25	Positive	Acetochlor-d11
Flufenacet	364.3	16.4	95	152/20	194.1/9	Positive	Acetochlor-d11
Isoxaflutole	360	15.6	130	251/20	79/16	Positive	Atrazine-d5
Mefenacet	299.1	15.8	95	148.1/12	120.1/32	Positive	Acetochlor-d11
Clodinafop-propargyl	350.1	16.9	110	266.1/16	238.1/24	Positive	Indoxacarb-d3
Clofibric acid-d4	216.9	14.8	78	131/17	85/5	Negative	–
Haloxfop-r-methyl	376	17.4	75	316/28	288/8	Positive	Acetochlor-d11
Quizalofop-p-	373.1	17.8	90	299/20	271/28	Positive	Acetochlor-d11

ethyl							
Imazaquin	312.1	13.4	130	181/44	199/24	Positive	Atrazine-d5
Imazethapyr	290.1	12.7	130	177/32	245/24	Positive	Atrazine-d5
Butralin	296.1	18.7	90	240/13	222.1/25	Positive	Nicosulfuron-d6
Carfentrazone-ethyl	412	16.7	150	346/28	366/20	Positive	Imidacloprid-d4
Pinoxaden	401.2	16.6	110	317.2/21	289.2/40	Positive	Acetoclor-d11
Fluazinam	384.1	18.3	140	282.1/20	328.1/16	Positive	Acetoclor-d11
Fluroxypyr	253	13.2	70	194.9/12	232.9/5	Negative	Carbaryl-d7
Metribuzin	215.3	13.7	120	187.1/17	145/21	Positive	Atrazine-d5
Amicarbazone	242.2	13.0	65	143.1/12	55.2/32	Positive	Atrazine-d5
Florasulam	360.15	13.9	120	129.1/25	191.9/17	Positive	Isoproturon-d6
Penoxsulam	484.2	14.6	170	195.1/32	164.1/40	Positive	Atrazine-d5
Mesotrione	340.1	13.7	140	228/17	104/37	Positive	Atrazine-d5
Fomesafen	437	16.0	155	194.9/40	222/36	Negative	Acetoclor-d11
Napropamide	272.2	16.0	155	171.1/20	129.1/16	Positive	Acetoclor-d11
Propyzamide	256	16.0	75	190/12	173/24	Positive	Acetoclor-d11
2,4-D	219	14.5	105	160.9/16	175/4	Negative	Clofibric acid-d4
MCPA	199	14.3	95	141/17	155/5	Negative	Clofibric acid-d4
Bentazone	239	14.0	120	132/29	197/21	Negative	Carbofuran-d3
Propham	180.1	14.9	80	138/5	120/15	Positive	Isoproturon-d6
Pendimethalin	282	18.6	100	212/9	194/21	Positive	Acetoclor-d11
Propoxur	210.1	13.9	65	111/13	168.1/5	Positive	Carbofuran-d3
Carbofuran	222.3	13.9	80	165.1/12	123.1/24	Positive	Carbofuran-d3
Carbofuran-d3	225.3	13.9	95	165.2/12	123.2/24	Positive	–
3-hydroxy-carbofuran	238	11.7	110	163/16	220/4	Positive	Carbaryl-d7
Aldicarb	213.1	13.0	110	89.1/20	116.1/12	Positive	Carbofuran-d3
Aldicarb-sulfone	223.1	10.2	110	86/15	148/10	Positive	Carbofuran-d3
Aldicarb-sulfoxide	207	9.2	80	132/5	89/5	Positive	Carbofuran-d3
Carbaryl	202.1	14.2	70	145.1/8	127.1/36	Positive	Carbaryl-d7
Carbaryl-d7	209.1	14.2	95	133.1/36	152.8/8	Positive	–
Diethofencarb	268.1	15.5	55	226.1/5	124/37	Positive	Tebuconazole-d9
Fenobucarb	208.1	15.4	95	95/13	151.1/5	Positive	Tebuconazole-d9
Indoxacarb	528	17.5	110	249/13	218/25	Positive	Indoxacarb-d3
Indoxacarb-d3	531.2	17.5	129	249.2/16	293.2/12	Positive	–
Isoprocab	194.1	14.6	100	95/13	95/13	Positive	Tebuconazole-d9
Methomyl	163	10.5	70	88.1/5	106.1/12	Positive	Carbofuran-d3
Pirimicarb	239.2	11.5	105	72/25	182.2/17	Positive	Carbofuran-d3
Acetamiprid	223.1	12.2	110	126/25	56.2/17	Positive	Acetamiprid-d3
Acetamiprid-d3	226.2	12.2	114	126.1/24	90.2/44	Positive	–
Clothianidin	250	11.7	60	169.1/13	131.9/20	Positive	Imidacloprid-d4
Dinotefuran	203.1	9.4	80	129.1/9	114.1/13	Positive	Atrazine-desethyl-d7
Imidacloprid	256.1	11.9	115	209/17	210.1/9	Positive	Imidacloprid-d4
Imidacloprid-d4	260.2	11.9	130	87/20	179.3/20	Positive	–
Thiacloprid	253	12.8	95	126/21	90/40	Positive	Acetamiprid-d3
Thiamethoxam	292	11.0	90	211/12	181/24	Positive	Acetamiprid-d3

Diazinon	305.1	17.3	120	169.1/20	153.2/24	Positive	Atrazine-d5
Profenofos	373	17.8	130	345/24	302.9/20	Positive	Tebuconazole-d9
Dichlorvos	221	13.5	120	109/15	145/15	Positive	Atrazine-d5
Dimethoate	230	12.0	60	199/8	125/24	Positive	Carbendazim-d3
Isofenphos-methyl	332.1	17.2	80	231/16	273.05/0	Positive	Atrazine-d5
Malathion	331	16.2	110	127.1/12	99/28	Positive	Tebuconazole-d9
Omethoate	214.1	8.0	85	183/8	125/24	Positive	Oaethoate-d3
Omethoate-d3	217.1	8.0	90	125/24	183/8	Positive	–
Tolfenpyrad	384.2	17.9	170	197.1/29	170.9/25	Positive	Tebuconazole-d9
Chlorobenzuron	307	16.4	120	154/8	126/32	Negative	Atrazine-d5
Etoxazole	360.2	18.8	135	141/33	304.1/17	Positive	Tebuconazole-d9
Pyriproxyfen	322.1	18.3	105	96/25	185/25	Positive	Tebuconazole-d9
Tebufenozide	353.2	16.6	60	133/21	297.2/5	Positive	Tebuconazole-d9
Cyproconazole	292.1	15.3	100	70/20	125/36	Positive	Tebuconazole-d9
Difenoconazole	406.1	16.8	145	251/28	337.1/16	Positive	Acetoclor-d11
Diniconazole	326.1	16.3	160	70/29	159/37	Positive	Tebuconazole-d9
Epoxiconazole	330.1	15.7	115	121/25	101/40	Positive	Atrazine-d5
Flusilazole	316.1	15.9	145	247.1/20	165/28	Positive	Tebuconazole-d9
Myclobutanil	289.1	15.6	130	70.1/20	125/40	Positive	Tebuconazole-d9
Propiconazol	342.1	16.4	170	159/37	205/17	Positive	Tebuconazole-d9
Tebuconazole	308	15.7	95	125/40	151/40	Positive	Tebuconazole-d9
Tebuconazole-d9	317.3	15.8	115	70.2/ 24	151/ 32	Positive	–
Triadimefon	294.1	15.8	110	69.2/20	197/16	Positive	Tebuconazole-d9
Triadimenol	296.1	15.1	85	70.1/21	99/17	Positive	Tebuconazole-d9
Triazophos	314.1	16.3	105	119.1/20	162.1/20	Positive	Tebuconazole-d9
Tricyclazole	190	12.2	135	163/25	136/33	Positive	Tebuconazole-d9
Azoxystrobin	404.13	15.6	130	372.1/12	344.2/28	Positive	Atrazine-d5
Fluoxastrobin	459.09	16.2	140	427.2/16	188/40	Positive	Acetoclor-d11
Kresoxim-methyl	314.14	16.8	75	267.1/0	222.1/12	Positive	Tebuconazole-d9
Picoxystrobin	368.11	16.8	80	205.1/4	145/24	Positive	Tebuconazole-d9
Pyraclostrobin	388.11	17.2	110	194/8	163/24	Positive	Tebuconazole-d9
Trifloxystrobin	409.14	17.7	115	186/16	206/12	Positive	Tebuconazole-d9
Prochloraz	376.04	15.5	95	308/8	70/28	Positive	Tebuconazole-d9
Triflumizole	346.1	16.6	85	278.1/8	73.1/16	Positive	Tebuconazole-d9
Imazalil	297.06	12.8	130	158.9/28	255/20	Positive	Atrazine-d5
Cyprodinil	226.14	15.6	155	93.1/40	108.1/28	Positive	Tebuconazole-d9
Pyrimethanil	200.1	14.4	130	107/28	183/28	Positive	Tebuconazole-d9
Carbendazim	192	9.7	140	160/20	132/36	Positive	Carbendazim-d3
Carbendazim-d3	195.1	9.7	130	160.1/20	132.1/36	Positive	–
Thiophanate-methyl	343.1	13.5	145	151/21	160/37	Positive	Carbofuran-d3
Boscalid	343.04	15.8	130	307.1/21	271.1/36	Positive	Acetoclor-d11
Dimethomorph	388.13	14.9	155	301.1/20	165/36	Positive	Clofibric acid-d4
Metalaxyl	280.16	14.3	105	220.1/12	192.1/20	Positive	Tebuconazole-d9
Oxathiapiprolin	540	16.0	180	500.2/30	163/50	Positive	Tebuconazole-d9
Isoprothiolane	291.1	16.3	65	231/9	189/25	Positive	Acetoclor-d11

Table S2 Information on treatment process and capacity of WWTPs

Abbreviation	Treatment process	Treatment capacity (m3)		
		Total	Domestic wastewater	Industrial wastewater
W1	A2O	3,583,100	3,224,800	358,300
W2	A2O	3,382,000	3,382,000	0
W3	SBR	1,768,400	1,768,400	0
W4	A2O	1,492,300	1,338,400	153,900
W5	A2O+O3	21,057,000	20,043,000	1,014,000
W6	Anaerobic+Carrousel oxidation ditch+High density settling tank+V-type Filter+UV+constructed wetlands	28,470,000	28,325,000	145,000
W7	A2O	1,920,000	1,920,000	0
W8	CAST	5,196,500	4,604,500	592,000
W9	Anaerobic+Carrousel oxidation ditch	26,660,000	25,212,000	1,448,000
IW1	A/O	8,496,000	0	8,496,000
IW2	A2/O	217,200	0	217,200
IW3	A/O	4,011,000	0	4,011,000

Table S3 Relative recoveries (%) of each pesticide on the four onine SPE cartridges

Chemical name	SB-Aq		BonusRP		Phenyl-Hexyl		PLRP-s	
	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD
Paclbutrazol	101	1.7	102	3.4	106	3.9	101	2.2
Acetochlor	93	2.9	93	5.2	98	3.9	95	1.5
Alachlor	91	2.4	91	1.0	98	1.2	97	2.5
Butachlor	93	2.6	98	1.7	105	2.3	98	3.4
Metolachlor	103	2.9	103	1.5	107	3.9	100	2.7
Pretilachlor	93	3.3	99	1.7	101	2.1	99	3.7
Ametryn	105	1.6	103	1.4	112	0.5	103	1.3
Atrazine	104	1.9	102	1.2	108	2.0	103	2.3
Atrazine-desethyl	2.8	0.4	116	4.6	97	5.1	109	2.4
Atrazine-desisopropyl	98	1.0	98	1.8	104	2.1	98	2.8
Cyanazine	75	3.3	75	1.7	100	2.1	94	4.6
Prometryn	102	1.3	103	1.2	106	1.4	100	0.9
Simazine	106	1.1	108	1.9	112	1.6	107	1.2
Terbuthylazine	106	1.7	107	1.3	110	2.4	102	1.9
Terbutryn	90	11	103	14.0	105	15	92	2.7
Bensulfuron-methyl	90	10	95	4.5	95	7.4	100	6.8
Ethametsulfuron-methyl	94	4.4	94	1.6	97	2.7	98	1.8
Nicosulfuron	90	1.4	90	2.0	92	1.6	98	1.9
Pyrazosulfuron-ethy	91	1.7	91	1.9	98	2.0	99	1.8
Tribenuron-methyl	92	1.7	93	0.4	96	1.7	97	2.4
Diflufenican	92	5.4	95	4.3	95	5.6	98	5.2
Diuron	103	0.6	103	2.9	107	3.7	105	0.8
Isoproturon	95	1.2	96	1.7	100	0.8	99	1.5

Chlortoluron	102	1.7	101	1.0	110	0.9	104	1.8
Flufenacet	98	2.4	99	1.9	98	3.1	99	2.3
Isoxaflutole	100	5.0	98	3.9	107	8.0	99	6.2
Mefenacet	104	2.4	108	4.3	106	3.3	101	4.1
Clodinafop-propargyl	91	2.2	96	8.2	99	3.0	96	2.0
Haloxypop-r-methyl	100	7.2	90	6.2	95	5.8	83	20
Quizalofop-p-ethyl	96	1.9	96	7.9	101	5.0	104	4.0
Imazaquin	96	2.3	95	1.3	104	2.0	100	1.5
Imazethapyr	102	2.3	101	1.6	106	2.4	103	1.6
Butralin	110	5.4	101	8.3	103	6.6	113	3.6
Carfentrazone-ethyl	94	2.9	104	3.5	104	4.5	105	3.0
Pinoxaden	91	3.6	97	2.0	99	5.0	97	7.1
Fluazinam	96	8.4	94	8.8	104	8.6	104	9.3
Fluroxypyr	91	2.3	92	3.9	94	3.2	95	4.4
Metribuzin	110	3.8	111	1.4	115	2.3	108	3.1
Amicarbazone	96	1.2	95	2.3	99	0.7	100	1.2
Florasulam	95	2.3	97	1.7	104	2.8	101	1.8
Penoxsulam	96	4.4	97	3.4	101	3.3	100	1.4
Mesotrione	105	2.5	106	3.6	109	3.8	105	2.5
Fomesafen	132	6.7	90	3.3	98	2.9	93	4.4
Napropamide	107	2.5	110	2.9	108	2.6	103	3.1
Propyzamide	103	1.7	101	2.6	108	3.7	101	4.5
2,4-D	111	7.2	91	3.7	101	4.5	101	7.4
MCPA	99	2.9	94	3.1	99	2.7	98	2.9
Bentazone	108	2.4	94	2.7	103	1.6	97	2.1
Propham	106	1.5	103	4.4	109	5.1	103	2.1
Pendimethalin	99	6.5	91	2.5	113	6.1	101	3.7
Diazinon	101	2.5	103	1.2	108	1.5	101	2.4
Propoxur	99	1.0	101	2.1	108	2.0	104	2.0
Carbofuran	95	0.8	96	0.9	103	1.0	102	1.3
3-hydroxy-carbofuran	103	2.7	98	2.7	96	1.7	100	1.6
Aldicarb	107	1.7	110	2.5	122	4.0	114	5.9
Aldicarb-sulfone	0.1	0.03	0.8	0.1	0.8	0.2	92	3.6
Aldicarb-sulfoxide	2.8	0.3	3.0	0.4	2.9	0.2	60	6.0
Carbaryl	94	2.1	95	2.6	103	1.9	99	1.8
Diethofencarb	95	4.4	98	3.3	99	3.9	97	3.0
Fenobucarb	96	2.2	99	2.9	103	1.8	98	2.3
Indoxacarb	102	20	112	12.3	100	20	108	22
Isoprocarb	95	1.1	99	1.5	105	2.3	98	2.7
Methomyl	0.1	0.02	1.5	0.1	0.2	0.0	101	0.9
Pirimicarb	3.0	0.2	101	0.8	107	1.3	100	1.6
Acetamiprid	103	2.4	96	2.2	100	1.1	100	3.1
Clothianidin	99	5.8	101	1.8	96	3.2	100	1.3
Dinotefuran	0.5	0.2	1.5	0.5	1.4	0.3	20	3.9
Imidacloprid	78	3.9	98	2.6	96	2.9	98	3.0
Thiacloprid	95	1.8	95	1.6	100	2.2	102	1.8
Thiamethoxam	0.3	0.1	86	2.0	92	3.0	102	3.4
Profenofos	99	4.9	97	1.2	101	5.4	102	6.3
Dichlorvos	75	1.2	77	3.2	98	3.2	95	7.3

Dimethoate	1.0	0.1	97	1.8	100	0.7	100	1.6
Isofenphos-methyl	100	3.6	101	5.4	96	8.8	100	7.0
Malathion	102	2.3	106	0.5	104	3.5	100	2.9
Omethoate	0.1	0.05	0.7	0.1	0.1	0.1	19	3.5
Tolfenpyrad	108	23	119	18	107	19	109	25
Chlorobenzuron	100	4.4	98	6.1	107	8.2	108	5.5
Etoxazole	110	10	102	9.5	115	8.8	108	14
Pyriproxyfen	113	7.6	109	7.3	106	5.6	102	6.2
Tebufenozide	99	1.6	102	1.3	103	1.6	100	2.3
Cyproconazole	102	1.6	102	2.6	107	1.7	102	2.7
Difenoconazole	94	3.5	95	1.6	97	1.6	101	3.2
Diniconazole	103	5.0	107	3.3	108	1.9	101	3.2
Epoxiconazole	112	4.8	111	4.4	117	5.0	106	2.3
Flusilazole	102	3.3	103	1.8	103	1.5	100	3.6
Myclobutanil	97	3.1	97	2.0	105	1.8	98	2.1
Propiconazol	102	2.7	103	3.2	104	2.8	101	2.8
Tebuconazole	112	4.8	111	4.4	117	5.0	106	2.3
Triadimefon	108	1.0	106	2.5	109	1.6	102	4.2
Triadimenol	99	1.1	98	3.0	104	0.6	99	1.2
Triazophos	97	0.8	100	1.2	101	1.9	99	1.2
Tricyclazole	104	2.1	99	2.3	105	1.2	100	2.9
Azoxystrobin	91	2.5	96	2.9	100	1.9	96	1.5
Fluoxastrobin	90	0.8	98	1.7	97	3.0	97	3.8
Kresoxim-methyl	91	1.5	93	4.2	96	1.9	96	3.2
Picoxystrobin	94	2.6	101	1.7	100	0.8	100	2.1
Pyraclostrobine	89	5.4	92	6.5	91	9.2	93	7.4
Trifloxystrobin	77	2.2	84	3.4	92	2.2	101	3.5
Prochloraz	92	3.3	96	2.1	97	2.0	100	1.9
Triflumizole	91	4.7	92	2.1	99	1.8	100	4.2
Imazalil	98	1.0	99	3.4	109	1.6	100	2.2
Cyprodinil	103	1.2	104	0.9	107	2.2	103	1.5
Pyrimethanil	100	2.1	100	1.1	104	1.8	102	1.0
Carbendazim	0.4	0.1	2.1	0.1	4.4	0.2	102	2.9
Thiophanate-methyl	110	2.8	112	7.6	113	4.1	103	3.4
Boscalid	106	2.1	105	3.7	111	3.5	104	2.3
Dimethomorph	83	2.7	84	4.4	91	2.5	104	16
Metalaxyl	94	1.2	95	1.9	100	0.7	99	0.7
Oxathiapiprolin	100	2.0	99	3.4	97	1.9	105	7.9
Isoprothiolane	99	1.1	102	2.2	103	2.6	100	2.0

Table S4 Influence of MeOH contents in loading/wash solvent on the analyte recoveries (%; n=5)

Chemical name	0% MeOH		2% MeOH		5% MeOH		10% MeOH		15% MeOH	
	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD
Paclobutrazol	101	2.0	92	11.0	97	0.8	94	2.4	88	12.1
Acetochlor	94	2.5	102	2.8	102	7.4	99	6.5	98	3.5
Alachlor	97	2.4	94	7.8	100	4.0	96	7.2	102	0.2
Butachlor	98	3.1	92	1.9	96	1.5	93	3.6	95	4.6
Metolachlor	100	2.6	106	4.9	110	7.3	103	0.9	106	8.0
Pretilachlor	99	3.4	94	2.5	97	0.5	95	2.5	93	2.0
Ametryn	103	1.2	103	1.4	105	1.4	104	2.1	102	1.5
Atrazine	103	2.1	103	1.1	102	0.2	102	2.1	99	3.5
Atrazine-desethyl	110	2.3	107	2.4	106	7.5	96	4.5	105	4.0
Atrazine-desisopropyl	98	2.5	96	1.7	98	2.5	98	3.7	96	2.1
Cyanazine	95	4.5	95	1.9	91	2.6	84	7.9	90	4.6
Prometryn	100	0.8	101	2.1	98	0.5	99	2.4	101	0.2
Simazine	107	1.2	106	1.3	106	1.2	107	2.9	105	0.5
Terbuthylazine	102	2.1	98	1.6	100	3.7	101	0.5	100	0.8
Terbutryn	92	2.5	95	1.1	92	1.8	93	0.6	94	1.8
Bensulfuron-methyl	100	6.4	94	0.6	90	2.1	89	0.6	85	4.0
Ethametsulfuron-methyl	98	2.2	96	5.8	91	1.6	87	2.1	90	1.9
Nicosulfuron	98	1.7	94	3.4	90	4.4	88	4.2	94	1.1
Pyrazosulfuron-ethy	99	2.5	100	2.3	100	2.2	98	2.1	97	1.6
Tribenuron-methyl	97	2.1	98	2.6	93	2.0	86	2.8	82	1.3
Diflufenican	98	4.7	83	2.1	95	4.0	87	3.9	90	4.6
Diuron	106	2.3	99	1.6	99	3.4	96	1.9	97	0.5
Isoproturon	99	1.4	98	1.5	98	3.0	96	1.1	98	0.7
Chlortoluron	104	1.6	103	1.3	101	0.4	97	0.9	95	4.1
Flufenacet	99	2.0	101	6.8	98	3.1	99	3.2	103	1.8
Isoxaflutole	100	6.1	90	2.9	91	5.8	86	10	98	1.8
Mefenacet	100	3.7	101	4.0	98	0.6	105	8.6	104	6.8
Clodinafop-propargyl	95	2.6	91	3.3	86	13	79	12	92	3.0
Haloxypop-r-methyl	94	4.2	95	6.5	88	4.6	93	3.6	83	2.5
Quizalofop-p-ethyl	103	4.0	101	4.6	106	4.7	103	7.2	113	1.3

Imazaquin	100	1.5	100	0.8	98	4.2	91	4.0	101	2.9
Imazethapyr	103	1.4	103	1.5	106	2.5	101	1.8	104	4.3
Butralin	114	3.7	102	14	91	2.6	86	13	86	9.0
Carfentrazone-ethyl	104	3.0	100	4.1	86	17	88	13	96	1.4
Pinoxaden	98	6.7	97	6.0	96	11	94	10	100	2.3
Fluazinam	104	8.4	95	5.2	113	1.9	109	2.0	109	5.2
Fluroxypyr	97	3.7	95	7.9	101	3.4	104	5.6	96	5.6
Metribuzin	108	3.3	105	3.6	102	2.8	101	3.5	104	0.2
Amicarbazone	100	1.1	98	2.5	98	2.5	95	2.1	97	2.6
Florasulam	101	1.7	104	2.1	100	3.5	102	1.9	98	2.9
Penoxsulam	101	1.8	100	2.5	97	1.5	95	1.6	98	1.0
Mesotrione	105	2.5	102	7.7	105	9.2	100	8.9	94	7.5
Fomesafen	100	3.2	111	7.3	106	4.2	109	8.5	94	23
Napropamide	103	3.0	98	4.3	97	3.6	97	4.1	94	7.8
Propyzamide	101	4.0	99	3.1	98	5.5	100	4.3	99	5.2
2,4-D	99	8.0	103	7.1	102	0.9	99	2.9	102	1.9
MCPA	97	3.3	100	11	100	0.9	96	8.6	101	5.7
Bentazone	98	3.6	99	2.0	98	1.6	99	6.5	100	7.3
Propham	103	1.9	107	4.6	112	5.9	105	8.2	114	5.8
Pendimethalin	102	4.0	99	3.2	87	9.2	94	5.4	82	24
Propoxur	104	1.8	107	1.9	106	3.1	104	0.1	106	0.5
Carbofuran	101	1.4	103	2.2	102	5.2	99	0.9	100	0.8
3-Hydroxy-carbofuran	101	2.7	101	1.7	98	9.4	91	4.0	98	1.9
Aldicarb	113	5.6	108	2.2	111	2.9	115	4.9	120	5.2
Aldicarb-sulfone	92	3.2	85	2.8	73	1.5	39	3.6	8.7	0.1
Aldicarb-sulfoxide	59	6.2	21	0.1	11	1.0	4.8	0.6	2.7	0.1
Carbaryl	99	1.7	103	5.5	99	8.7	92	5.1	96	0.8
Diethofencarb	96	2.9	98	2.1	94	3.3	100	4.9	97	1.9
Fenobucarb	97	2.3	96	2.2	94	8.0	94	4.1	94	7.9
Indoxacarb	107	20	121	2.2	125	13	125	18	128	2.1
Isoprocab	99	3.3	94	6.0	90	7.1	101	1.4	90	4.6
Methomyl	101	1.0	99	1.8	95	1.5	84	0.8	54	1.7
Pirimicarb	100	1.7	100	2.7	101	0.8	101	0.8	99	0.5

Acetamiprid	100	2.8	99	1.6	101	1.1	99	3.8	102	1.3
Clothianidin	100	1.9	99	4.7	99	1.1	97	4.1	94	1.8
Dinotefuran	19	4.0	10	0.9	6.2	1.0	2.9	0.2	1.8	0.2
Imidacloprid	98	2.7	93	0.8	93	8.9	83	3.7	93	0.1
Thiacloprid	101	1.9	102	3.7	95	5.1	90	2.4	99	0.2
Thiamethoxam	101	3.5	104	1.6	104	3.1	92	7.8	91	2.5
Diazinon	101	2.3	97	1.9	95	1.0	99	2.2	95	2.9
Profenofos	103	6.1	99	5.0	100	2.7	100	9.5	104	7.3
Dichlorvos	96	6.8	100	2.8	114	28	123	20	97	0.8
Dimethoate	100	1.5	98	1.5	97	4.0	96	2.6	97	1.6
Isofenphos-methyl	100	6.2	80	6.0	75	3.1	76	2.2	81	2.2
Malathion	100	2.6	99	3.0	96	9.2	92	11	98	2.6
Omethoate	18	3.7	9.2	0.5	5.3	0.8	2.3	0.6	1.5	0.9
Tolfenpyrad	107	23	111	12	177	28	224	11	240	6.9
Chlorobenzuron	108	4.9	120	5.3	120	3.7	127	4.4	119	1.4
Etoxazole	107	13	112	2.2	117	1.2	118	1.3	119	6.8
Pyriproxyfen	102	5.6	102	1.1	107	5.5	113	0.7	119	0.7
Tebufenozide	100	2.1	97	0.0	96	2.3	98	0.3	96	2.4
Cyproconazole	102	2.4	99	2.0	99	2.4	97	2.6	98	1.0
Difenoconazole	101	2.9	103	1.6	104	3.6	107	2.5	109	2.1
Diniconazole	102	2.9	97	5.3	94	3.3	98	2.3	95	8.4
Epoxiconazole	105	3.4	100	4.7	97	1.1	103	5.1	108	6.3
Flusilazole	94	4.6	91	5.4	94	8.6	98	5.0	97	2.3
Myclobutanil	97	2.6	87	1.3	85	4.1	90	1.8	87	1.6
Propiconazol	101	2.6	103	3.6	102	1.8	102	4.7	99	1.3
Tebuconazole	105	3.4	139	6.6	134	1.5	142	7.0	150	8.7
Triadimefon	102	3.9	97	4.2	101	2.1	100	5.7	98	5.0
Triadimenol	99	1.1	97	1.5	96	2.5	98	1.4	97	2.6
Triazophos	99	1.0	99	3.8	100	3.6	102	1.3	106	2.5
Tricyclazole	99	2.8	96	0.7	99	2.4	95	1.1	100	0.0
Azoxystrobin	97	1.9	95	2.9	95	3.3	96	3.4	97	5.9
Fluoxastrobin	92	7.5	88	2.9	89	3.3	92	2.1	92	3.4
Kresoxim-methyl	97	3.0	97	2.7	98	4.1	94	3.0	96	1.7

Picoxystrobin	100	1.9	98	3.7	97	2.0	97	0.8	96	4.9
Pyraclostrobine	94	7.3	91	8.2	95	11	103	3.9	91	2.5
Trifloxystrobin	102	3.6	99	0.8	101	4.3	103	7.0	100	1.2
Prochloraz	99	2.3	90	9.6	92	7.5	101	2.0	95	11
Triflumizole	99	3.8	96	1.9	100	1.5	102	3.1	100	1.9
Imazalil	100	2.3	103	3.9	104	9.5	104	3.7	103	0.9
Cyprodinil	103	1.4	100	2.2	100	2.0	101	1.7	100	1.2
Pyrimethanil	102	0.9	100	0.3	100	1.0	98	1.3	98	0.1
Carbendazim	102	2.7	99	1.0	96	2.8	82	1.4	47	2.8
Thiophanate-methyl	102	3.6	101	3.6	93	8.2	88	6.8	97	6.2
Boscalid	103	2.2	94	3.4	94	2.8	96	5.0	98	2.2
Dimethomorph	103	15	102	2.1	100	3.3	98	1.4	96	2.0
Metalaxyl	98	1.1	99	0.5	100	4.5	99	1.8	97	1.0
Oxathiapiprolin	105	7.1	104	3.1	112	1.5	115	1.4	115	5.2
Isoprothiolane	100	1.9	99	1.8	99	2.1	102	3.0	99	0.2

Table S5 Influence of wash volume on the analyte recoveries (%)

Chemical name	0 mL		0.5 mL		1 mL		1.5 mL		2 mL		2.5 mL		3 mL		4 mL	
	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD	Recovery	SD
Paclobutrazol	100	1.6	110	0.7	88	1.3	90	0.7	89	2.4	99	0.7	95	7.9	103	1.2
Acetochlor	100	1.0	97	0.5	91	2.1	95	0.3	92	0.7	98	0.4	95	3.9	95	0.1
Alachlor	100	0.7	100	1.4	94	1.1	96	3.5	93	4.0	93	2.7	94	1.2	97	1.0
Butachlor	100	4.3	97	0.2	100	3.3	99	1.1	98	0.1	102	0.1	97	1.4	99	3.8
Metolachlor	100	3.2	97	4.3	101	6.4	102	4.4	94	0.9	95	4.8	95	4.6	94	3.1
Pretilachlor	100	1.0	102	3.1	97	3.3	98	1.9	101	4.5	102	1.1	104	1.2	105	5.5
Ametryn	100	0.1	97	0.6	94	0.3	94	2.0	97	0.8	98	1.6	99	0.7	100	0.7
Atrazine	100	4.3	101	3.2	102	0.6	104	1.1	103	1.7	105	0.4	104	2.9	103	6.1
Atrazine-desethyl	100	2.5	95	1.7	94	0.1	94	1.2	92	2.5	96	5.3	100	4.5	104	0.1
Atrazine-desisopropyl	100	1.9	100	0.7	99	1.2	97	4.7	99	1.7	101	0.1	102	1.8	102	1.0
Cyanazine	100	0.3	102	1.9	96	3.8	104	2.5	98	0.1	98	0.5	102	4.7	102	3.3
Prometryn	100	1.0	104	0.5	100	2.6	106	2.2	101	0.8	103	1.4	101	2.7	104	1.0
Simazine	100	0.4	101	3.2	101	0.7	99	0.1	100	0.3	99	1.7	99	1.8	102	0.1
Terbuthylazine	100	4.2	95	1.2	96	2.2	96	1.3	99	3.1	97	1.3	101	1.1	102	1.3
Terbutryn	100	1.3	98	0.5	96	2.1	101	1.0	102	0.8	104	0.5	101	0.2	106	0.7
Bensulfuron-methyl	100	4.2	97	2.9	91	1.0	91	1.0	94	0.8	93	0.4	90	1.6	93	3.4
Ethametsulfuron-methyl	100	4.1	102	0.9	98	0.5	99	0.7	102	1.6	100	3.5	95	0.7	99	2.2
Nicosulfuron	100	5.8	97	0.5	96	2.2	97	3.0	102	2.6	100	1.0	95	0.2	96	3.6
Pyrazosulfuron-ethy	100	0.3	98	0.4	99	0.5	106	1.5	101	1.1	100	1.6	99	1.6	100	1.0
Tribenuron-methyl	100	4.0	102	1.3	99	0.8	97	1.3	98	1.5	99	2.5	97	0.8	93	2.9
Diflufenican	100	2.9	91	6.4	97	3.2	97	0.9	94	12	100	3.8	101	11	105	6.7
Diuron	100	0.9	107	2.8	100	6.8	94	1.0	99	7.2	97	0.9	101	6.6	109	3.6
Isoproturon	100	2.0	105	6.6	99	7.8	99	2.2	99	3.8	100	2.0	103	1.1	102	2.6

Chlortoluron	100	0.3	98	0.3	97	0.5	99	0.1	98	4.1	99	0.5	99	0.6	101	0.1
Flufenacet	100	2.3	99	0.1	100	2.2	98	1.5	101	1.1	102	0.7	100	2.1	101	3.0
Isoxaflutole	100	2.2	106	0.4	106	8.5	98	17	117	10	102	6.0	111	14	116	5.1
Mefenacet	100	3.2	110	2.8	102	4.6	104	2.8	109	3.0	105	2.1	101	0.8	103	2.3
Clodinafop-propargyl	100	3.1	108	2.3	103	2.8	102	4.8	104	1.2	100	1.7	108	4.8	105	4.7
Haloxypop-r-methyl	100	2.5	102	13	106	17	102	6.9	97	2.9	107	0.5	99	10	103	1.3
Quizalofop-p-ethyl	100	3.3	96	3.5	88	0.6	95	3.8	93	2.8	98	1.9	100	0.6	104	7.0
Imazaquin	100	0.2	106	3.4	101	1.2	103	6.1	106	0.9	106	1.0	106	0.4	104	4.5
Imazethapyr	100	0.2	102	3.4	101	1.3	100	5.3	106	3.1	107	0.3	107	0.2	107	0.004
Butralin	100	0.1	95	9.0	94	7.4	97	1.4	88	18	103	4.1	97	9.9	108	9.9
Carfentrazone-ethyl	100	0.0	109	1.0	104	3.2	104	4.9	108	2.1	106	1.9	102	2.2	110	4.0
Pinoxaden	100	2.3	99	3.1	101	3.7	99	1.1	98	1.6	95	2.1	97	2.6	97	2.0
Fluazinam	100	3.0	97	0.3	91	4.8	87	2.8	104	8.6	110	5.4	107	6.4	114	7.7
Fluroxypyr	100	0.1	99	5.0	90	3.5	92	6.6	96	4.4	103	4.8	92	13	99	3.2
Metribuzin	100	6.3	101	5.5	98	0.1	98	4.3	99	3.2	102	1.7	100	7.0	101	2.0
Amicarbazone	100	3.7	96	1.6	92	1.1	93	1.6	96	0.5	99	3.7	95	0.9	96	1.4
Florasulam	100	0.4	98	0.04	98	1.3	100	1.1	97	1.0	101	4.7	98	1.9	98	1.8
Penoxsulam	100	2.3	99	2.9	98	4.6	94	0.4	99	1.7	99	6.0	95	3.2	94	0.0
Mesotrione	100	11	102	3.9	92	3.6	98	1.9	106	1.0	100	5.0	98	6.3	103	2.2
Fomesafen	100	0.5	93	7.6	91	2.1	96	4.1	93	7.2	93	6.6	91	1.4	91	2.0
Napropamide	100	0.7	92	0.8	92	0.2	97	3.4	98	0.8	95	0.9	93	0.9	99	2.4
Propyzamide	100	3.6	101	0.2	96	1.1	97	1.6	100	4.1	105	2.8	104	4.0	101	6.3
2,4-D	100	1.9	112	1.5	107	3.9	105	12	111	4.1	113	0.03	106	1.8	109	5.2
MCPA	100	3.9	100	4.4	96	4.6	101	0.9	99	2.2	100	2.1	101	3.5	98	2.1
Bentazone	100	2.2	97	7.4	93	2.5	93	9.8	98	3.5	99	1.2	100	2.7	96	2.5
Propham	100	0.1	105	9.2	97	2.0	107	8.5	101	8.3	96	2.3	104	9.8	106	7.2
Pendimethalin	100	40	26	2.2	18	11	7.4	5.7	9.0	9.7	7.0	1.7	1.2	0.4	2.3	1.9
Propoxur	100	6.8	106	3.4	104	2.3	107	4.9	103	1.7	102	4.0	105	3.3	107	2.5

Carbofuran	100	0.1	102	1.0	103	0.1	104	5.1	104	2.2	99	3.0	100	2.1	101	3.5
3-Hydroxy-carbofuran	100	0.8	104	2.5	105	0.6	105	0.4	112	1.0	108	4.5	103	3.7	103	1.1
Aldicarb	100	0.6	107	5.5	104	0.04	108	0.5	97	4.5	103	5.5	112	10	121	3.9
Aldicarb-sulfone	100	4.0	102	0.3	87	0.01	70	2.2	75	28	83	0.03	23	1.4	25	17
Aldicarb-sulfoxide	100	20	63	1.2	13	1.6	3.1	0.2	3.0	0.8	2.1	0.4	0.4	0.0 2	1.1	0.4
Carbaryl	100	1.0	99	0.1	99	1.6	104	6.2	101	0.6	104	0.6	98	0.4	98	7.6
Diethofencarb	100	1.5	114	2.3	108	2.7	98	4.6	105	2.1	110	7.0	103	0.6	111	1.7
Fenobucarb	100	6.1	112	1.0	108	0.5	104	2.4	110	6.4	111	5.1	107	4.9	110	3.9
Indoxacarb	100	6.1	101	0.3	92	4.0	100	13	123	7.8	113	7.6	112	11	114	2.2
Isoprocarb	100	2.4	100	0.7	103	14	99	2.7	97	8.5	103	1.7	102	4.4	106	0.3
Methomyl	100	0.8	104	0.1	101	0.2	88	2.6	92	15	97	1.5	56	2.4	65	10
Pirimicarb	100	0.1	104	3.2	108	0.3	109	1.0	110	1.9	112	1.2	112	0.1	113	1.2
Acetamiprid	100	1.1	96	1.6	95	3.2	99	1.2	102	3.9	102	2.5	100	0.8	100	1.3
Clothianidin	100	3.0	106	9.9	98	1.6	103	0.5	107	5.6	109	0.2	107	2.0	110	2.4
Dinotefuran	100	11	52	1.6	10	0.2	2.9	0.1	2.2	0.4	1.6	0.5	0.8	0.3	0.4	0.2
Imidacloprid	100	3.8	97	0.8	97	2.0	99	0.4	100	3.2	103	0.5	103	2.7	103	0.6
Thiacloprid	100	0.7	104	2.6	100	0.8	99	3.7	101	0.5	102	4.7	107	9.7	102	0.9
Thiamethoxam	100	1.7	94	4.6	94	0.3	99	2.1	107	5.1	110	0.8	107	4.3	108	1.5
Diazinon	100	0.9	108	1.3	106	3.4	108	0.3	107	1.4	110	0.0	108	2.0	111	4.3
Profenofos	100	1.4	104	7.0	109	7.0	100	0.2	102	1.0	106	2.3	111	0.3	108	9.3
Dichlorvos	100	3.2	100	3.6	93	5.6	98	2.7	89	4.3	96	2.6	101	1.8	97	5.0
Dimethoate	100	1.4	102	1.0	105	1.9	106	0.5	106	3.0	106	2.9	105	1.1	103	2.2
Isofenphos-methyl	100	3.0	107	5.1	94	5.6	96	0.7	99	3.7	100	6.8	104	3.1	101	4.7
Malathion	100	3.3	100	3.6	102	2.5	98	4.1	101	0.1	101	3.4	97	1.2	98	3.2
Omethoate	100	22	42	4.6	7.4	0.7	1.8	0.2	1.4	0.9	1.2	0.4	0.2	0.0 2	0.5	0.2
Tolfenpyrad	100	36	141	18	143	22	168	2.2	211	16	264	22	287	6.4	327	15
Chlorobenzuro	100	2.7	104	2.2	100	4.4	100	6.1	95	3.0	101	4.6	105	2.6	101	3.4

n																
Etoazole	100	6.3	93	1.5	92	2.6	103	1.1	111	0.3	108	3.6	105	1.4	112	0.7
Pyriproxyfen	100	7.2	97	2.5	103	4.5	109	5.8	104	2.6	109	2.2	103	4.5	109	3.5
Tebufenozide	100	1.9	93	1.0	97	1.4	97	2.1	99	0.5	101	3.0	97	2.5	97	0.9
Cyproconazole	100	1.5	99	0.1	99	0.4	100	0.3	100	4.9	102	2.9	102	2.2	103	1.5
Difenoconazole	100	2.5	104	1.7	103	1.3	102	0.2	106	1.2	110	0.7	113	1.2	112	2.1
Diniconazole	100	0.9	104	6.6	97	5.5	103	1.2	98	4.7	103	3.0	101	1.8	109	2.8
Epoxiconazole	100	1.6	96	0.9	93	2.0	93	6.0	94	3.3	97	3.1	94	1.1	94	6.9
Flusilazole	100	2.1	103	0.1	94	2.7	106	1.9	100	2.4	101	1.8	100	0.4	100	1.5
Myclobutanil	100	4.9	95	0.7	97	0.1	94	1.1	97	4.9	106	9.6	95	7.8	94	1.4
Propiconazole	100	0.9	109	3.0	107	6.1	108	2.8	103	0.0	106	1.6	103	0.4	101	0.2
Tebuconazole	100	1.6	96	0.9	93	2.0	93	6.0	97	0.2	93	2.8	97	1.8	99	2.5
Triadimefon	100	1.3	101	7.7	97	0.7	97	0.3	104	0.1	100	5.6	100	3.8	101	2.0
Triadimenol	100	2.9	108	0.3	105	3.9	108	0.3	107	0.3	110	2.4	108	1.6	109	1.3
Triazophos	100	0.9	97	8.6	98	1.3	94	0.5	97	0.6	102	4.7	102	0.5	102	2.5
Tricyclazole	100	0.2	99	4.2	99	1.0	98	1.2	102	4.4	103	0.5	105	0.3	105	3.8
Azoxystrobin	100	2.6	99	1.3	91	5.1	88	1.0	89	1.3	92	2.7	94	3.6	99	2.8
Fluoxastrobin	100	0.6	97	6.0	95	0.4	97	1.9	97	2.7	105	1.6	98	0.8	98	1.3
Kresoxim-methyl	100	7.3	103	0.2	97	6.1	91	5.4	95	4.5	104	5.7	103	0.9	105	2.3
Picoxystrobin	100	5.9	97	3.7	98	0.6	99	1.1	97	1.4	101	2.4	100	3.7	100	0.6
Pyraclostrobin	100	2.0	103	7.0	92	3.8	95	4.8	99	3.3	98	1.9	100	2.4	102	0.6
Trifloxystrobin	100	4.0	99	0.5	97	0.5	99	3.6	102	0.4	104	2.0	105	4.8	105	1.6
Prochloraz	100	3.0	104	2.3	97	0.6	98	1.6	104	0.8	105	11	105	2.2	102	2.2
Triflumizole	100	0.6	100	3.2	96	5.4	98	1.0	100	0.3	99	0.4	101	1.1	103	3.0
Imazalil	100	2.2	100	3.3	97	3.8	100	3.8	100	1.7	100	0.5	101	1.6	101	1.7
Cyprodinil	100	1.7	105	1.3	106	0.2	109	0.5	105	6.1	107	4.5	101	2.2	104	4.8
Pyrimethanil	100	1.8	101	4.1	101	3.4	98	0.1	101	3.5	101	1.3	99	1.4	100	1.4
Carbendazim	100	2.6	105	1.6	101	0.7	94	0.4	98	13	101	1.7	66	0.1	66	20

Thiophanate-methyl	100	8.5	112	0.2	109	2.6	109	1.5	112	1.3	111	3.6	104	5.7	109	0.8
Boscalid	100	0.7	95	0.5	94	7.5	100	6.8	98	1.5	102	2.1	102	4.3	100	2.8
Dimethomorph	100	3.5	103	2.2	102	1.4	103	0.6	103	2.4	104	0.4	104	0.3	105	0.6
Metalaxyl	100	1.6	104	0.2	97	2.4	99	2.4	98	1.1	101	1.1	98	1.0	100	2.2
Oxathiapiprolin	100	3.3	100	9.1	99	0.5	102	2.3	103	7.6	103	1.0	103	14	101	1.1
Isoprothiolane	100	2.0	98	1.7	99	0.1	98	5.0	95	7.6	99	0.7	97	3.3	100	3.5

Table S6 Influence of loading/wash flowrate on the analyte recoveries (%)

Chemical name	0.5 mL/min	1 mL/min	1.5 mL/min	2 mL/min
Paclbutrazol	95	76	92	100
Acetochlor	99	100	96	100
Alachlor	96	89	92	100
Butachlor	95	98	100	100
Metolachlor	53	88	96	100
Pretilachlor	100	97	96	97
Ametryn	100	71	82	77
Atrazine	98	98	97	100
Atrazine-desethyl	76	86	94	100
Atrazine-desisopropyl	70	91	100	99
Cyanazine	84	46	100	97
Prometryn	83	81	94	100
Simazine	95	99	99	100
Terbutylazine	95	98	98	100
Terbutryn	68	89	99	100
Bensulfuron-methyl	87	96	100	91
Ethametsulfuron-methyl	100	93	97	91
Nicosulfuron	91	96	100	100
Pyrazosulfuron-ethy	97	93	97	100
Tribenuron-methyl	100	96	93	84
Diflufenican	72	82	92	100
Diuron	100	98	94	91
Isoproturon	89	91	99	100
Chlortoluron	100	99	96	92
Flufenacet	100	93	57	88
Isoxaflutole	100	89	83	86
Mefenacet	100	89	89	88
Clodinafop-propargyl	76	87	95	100
Haloxfop-r-methyl	100	64	97	92
Quizalofop-p-ethyl	100	79	80	82
Imazaquin	94	92	98	100
Imazethapyr	86	80	100	97
Butralin	86	90	100	89
Carfentrazone-ethyl	80	81	97	100
Pinoxaden	88	94	95	100
Fluazinam	100	90	97	94
Fluroxypyr	91	96	98	100
Metribuzin	100	93	94	93
Amicarbazone	100	90	80	78
Florasulam	94	99	100	98
Penoxsulam	100	95	88	89
Mesotrione	100	89	91	90
Fomesafen	94	88	100	100
Napropamide	75	78	91	100
Propyzamide	100	97	92	61
2,4-D	100	91	88	93
MCPA	89	96	95	100

Bentazone	100	98	97	95
Propham	100	93	88	83
Pendimethalin	100	91	94	84
Propoxur	89	97	100	96
Carbofuran	92	100	92	64
3-hydroxy-carbofuran	93	100	97	100
Aldicarb	48	59	86	100
Aldicarb-sulfone	12	74	89	100
Aldicarb-sulfoxide	100	92	94	88
Carbaryl	95	96	98	100
Diethofencarb	72	81	91	100
Fenobucarb	88	92	98	100
Indoxacarb	100	80	82	96
Isoprocarb	93	97	100	94
Methomyl	100	94	87	87
Pirimicarb	97	94	95	100
Acetamiprid	77	83	91	100
Clothianidin	75	85	96	100
Dinotefuran	91	88	96	100
Imidacloprid	100	94	98	94
Thiacloprid	100	93	85	80
Thiamethoxam	90	69	100	100
Diazinon	86	92	98	100
Profenofos	100	85	84	81
Dichlorvos	84	71	96	100
Dimethoate	79	100	91	84
Isofenphos-methyl	100	80	91	98
Malathion	88	94	96	100
Omethoate	91	98	100	95
Tolfenpyrad	100	71	45	99
Chlorobenzuron	79	98	100	99
Etoxazole	100	90	92	93
Pyriproxyfen	100	92	83	81
Tebufenozide	100	92	94	95
Cyproconazole	91	93	100	100
Difenoconazole	89	95	100	97
Diniconazole	87	88	95	100
Epoxiconazole	100	92	94	95
Flusilazole	89	100	86	88
Myclobutanil	98	98	87	100
Propiconazol	90	89	95	100
Tebuconazole	91	96	100	90
Triadimefon	97	100	99	95
Triadimenol	95	96	100	98
Triazophos	98	95	100	98
Tricyclazole	99	100	97	98
Azoxystrobin	86	90	93	100
Fluoxastrobin	91	95	95	100
Kresoxim-methyl	82	85	94	100

Picoxystrobin	100	89	95	92
Pyraclostrobine	85	89	95	100
Trifloxystrobin	93	92	96	100
Prochloraz	93	96	99	100
Triflumizole	91	93	99	100
Imazalil	94	93	100	100
Cyprodinil	98	100	96	92
Pyrimethanil	99	99	96	100
Carbendazim	42	90	98	100
Thiophanate-methyl	95	81	95	100
Boscalid	95	94	94	100
Dimethomorph	100	97	93	80
Metalaxyl	91	100	81	94
Oxathiapiprolin	1.7	17	71	100
Isoprothiolane	84	96	100	100

Table S7 Matrix effect (%) of all pesticides in the three matrixes

Chemical name	DW	SW	WWE
Paclobutrazol	104	64	50
Acetochlor	103	75	57
Acetochlor-d11	108	74	56
Alachlor	116	78	59
Butachlor	102	71	33
Metolachlor	113	69	52
Pretilachlor	109	72	46
Ametryn	112	64	59
Atrazine	105	62	57
Atrazine-d5	102	58	56
Atrazine-desethyl	94	56	32
Atrazine-desethyl-d7	96	57	34
Atrazine-desisopropyl	100	69	66
Cyanazine	112	49	41
Prometryn	113	64	62
Simazine	108	56	47
Terbuthylazine	109	69	57
Terbutryn	95	63	61
Bensulfuron-methyl	104	85	36
Ethametsulfuron-methyl	111	115	51
Nicosulfuron	115	119	71
Nicosulfuron-d6	115	112	73
Pyrazosulfuron-ethyl	110	72	35
Tribenuron-methyl	109	79	41
Di flufenican	96	76	62
Diuron	111	60	43
Isoproturon	97	73	50
Isoproturon-d6	103	70	52
Chlortoluron	119	48	32
Flufenacet	103	79	58
Isoxaflutole	117	62	49
Mefenacet	119	74	40
Clodinafop-propargyl	105	47	19.0
Clofibricacid-d4	102	38	24
Haloxypop-r-methyl	118	73	44
Quizalofop-p-ethyl	95	73	44
Imazaquin	116	67	57
Imazethapyr	112	68	65
Butralin	84	81	71
Carfentrazone-ethyl	103	47	11.0
Pinoxaden	114	76	28
Fluazinam	91	60	44
Fluroxypyr	82	44	14
Metribuzin	96	49	43
Amicarbazone	106	82	34
Florasulam	109	49	33
Penoxsulam	107	88	50

Mesotrione	99	47	37
Fomesafen	103	87	61
Napropamide	109	68	41
Propyzamide	109	77	54
2,4-D	90	42	21
MCPA	115	46	29
Bentazone	107	49	32
Propham	93	62	44
Pendimethalin	99	72	59
Propoxur	106	48	25
Carbofuran	107	52	26
Carbofuran-d3	101	54	27
3-hydroxy-carbofuran	106	41	15.0
Aldicarb	100	47	31
Aldicarb-sulfone	105	53	21
Aldicarb-sulfoxide	76	53	36
Carbaryl	99	54	18
Carbaryl-d7	106	51	18
Diethofencarb	98	74	48
Fenobucarb	91	74	50
Indoxacarb	116	69	16
Indoxacarb-d3	108	73	20
Isoprocarb	120	65	46
Methomyl	87	41	15
Pirimicarb	106	56	39
Acetamiprid	107	35	22
Acetamiprid-d3	111	32	22
Clothianidin	119	24	18
Dinotefuran	101	50	27
Imidacloprid	113	12	11
Imidacloprid-d4	104	13	12
Thiacloprid	95	40	29
Thiamethoxam	81	27	19.0
Diazinon	106	67	65
Profenofos	108	91	52
Dichlorvos	118	95	77
Dimethoate	104	38	29
Isofenphos-methyl	99	70	58
Malathion	101	64	30
Omethoate	91	66	22
Omethoate-d3	88	64	25
Tolfenpyrad	89	73	52
Chlorobenzuron	99	55	63
Etoxazole	87	87	70
Pyriproxyfen	81	77	56
Tebufenozide	107	76	58
Cyproconazole	110	84	64
Difenoconazole	107	73	57
Diniconazole	107	72	67

Epoxiconazole	113	72	51
Flusilazole	105	81	61
Myclobutanil	101	78	45
Propiconazol	120	74	66
Tebuconazole	113	84	57
Tebuconazole-d9	105	84	57
Triadimefon	105	86	58
Triadimenol	105	73	54
Triazophos	116	77	55
Tricyclazole	118	61	36
Azoxystrobin	107	80	46
Fluoxastrobin	108	75	47
Kresoxim-methyl	116	73	34
Picoxystrobin	103	76	63
Pyraclostrobine	107	69	48
Trifloxystrobin	101	73	33
Prochloraz	105	88	50
Triflumizole	102	76	54
Imazalil	104	68	63
Cyprodinil	106	74	56
Pyrimethanil	99	72	58
Carbendazim	98	60	38
Carbendazim-d3	101	56	34
Thiophanate-methyl	85	19	15
Boscalid	92	80	51
Dimethomorph	95	47	26
Metalaxyl	104	85	48
Oxathiapiprolin	98	81	37
Isoprothiolane	119	77	56

Table S8 Matrix spiking recovery (%) of every pesticide in the three matrixes (n=5)

Chemical name	DW								SW								WWE							
	5 ng/L		25 ng/L		100 ng/L		1000 ng/L		5 ng/L		25 ng/L		100 ng/L		1000 ng/L		5 ng/L		25 ng/L		100 ng/L		1000 ng/L	
	Rec				Rec		Rec		Rec		Rec		Rec		Rec		Rec		Rec		Rec		Rec	
	over	SD	Reco	SD	over	SD	over	SD	ove	SD	over	SD	over	SD	over	SD	ove	SD	over	SD	over	SD	over	SD
Paclobutrazol	107	8.6	94	3.0	97	2.1	98	1.8	91	4.3	102	4.4	89	5.6	96	9.5	79	2.5	88	6.9	105	5.2	102	2.6
Acetochlor	104	9.9	102	5.3	99	3.0	92	8.2	89	14	99	7.3	95	6.1	98	8.9	96	13	96	10	105	4.5	103	9.5
Alachlor	102	6.8	97	6.1	101	5.1	91	7.5	92	7.9	87	4.0	105	4.2	101	9.7	92	11	88	9.7	106	3.9	107	9.4
Butachlor	107	5.4	102	3.2	93	9.0	104	4.1	114	11	116	9.7	103	6.8	113	6.2	76	14	67	9	62	10	73	8
Metolachlor	110	6.1	99	6.2	94	4.0	101	2.0	86	9.2	108	15	86	7.5	106	3.0	108	8.3	92	10	102	11	105	6.2
Pretilachlor	111	7.4	99	2.3	103	8.6	99	1.7	107	7.2	110	8.0	117	7.8	108	6.5	106	14	97	13	102	17	95	16
Ametryn	99	2.9	99	5.0	89	2.8	98	1.2	121	1.8	118	6.5	94	3.7	110	2.3	115	6.0	112	1.4	103	2.2	103	2.0
Atrazine	94	4.4	102	2.9	91	2.5	101	0.4	106	20	108	13	98	7.5	110	1.4	100	13	102	4.9	99	3.5	101	1.7
Atrazine-desethyl	102	2.5	103	0.5	100	3.4	100	0.8	77	5.6	85	1.6	93	5.8	91	0.4	101	13	105	1.7	97	4.5	95	3.4
Atrazine-desisopropyl	88	7.9	98	3.7	88	3.7	97	1.5	108	14	115	7.6	112	6.3	118	3.3	95	10	103	4.3	121	5.4	113	2.5
Cyanazine	97	7.0	91	5.2	99	8.8	100	2.5	81	5.2	73	5.0	88	7.6	87	3.9	90	5.3	75	7.9	117	12	73	3.6
Prometryn	102	3.3	101	3.4	90	2.8	99	1.2	117	6.5	123	7.4	102	4.5	110	1.9	110	4.2	110	2.0	103	2.8	109	1.9
Simazine	94	3.6	97	3.0	87	2.8	93	1.3	96	6.0	93	2.6	86	3.7	91	2.1	80	8.5	80	2.5	86	1.1	78	2.5
Terbutylazine	93	1.5	97	3.1	85	2.7	97	3.8	105	5.8	103	7.3	95	6.4	117	2.0	89	3.0	87	2.9	95	5.1	99	3.3
Terbutryn	93	4.6	96	4.3	89	3.3	99	0.9	123	8.0	124	9.3	104	3.7	109	1.3	115	5.2	113	5.0	107	3.1	108	4.3
Bensulfuron-methyl	87	11	88	8.4	98	7.5	100	3.1	145	22	129	14	126	11	128	4.9	104	5.6	90	11	96	8.2	75	3.3
Ethametsulfuron-methyl	102	0.8	102	2.5	97	2.9	101	1.9	86	2.8	76	3.2	65	3.2	92	1.0	60	1.3	52	2.1	58	3.2	73	5.4
Nicosulfuron	100	2.9	99	4.1	99	1.7	97	1.6	114	7.6	98	2.8	97	1.8	91	1.1	100	1.7	94	2.0	103	1.5	99	5.4
Pyrazosulfuron-ethy	114	5.0	96	5.7	101	6.5	100	1.7	116	8.3	114	11	107	4.9	110	1.1	92	2.3	76	9.2	94	7.9	72	3.1
Tribenuron-methyl	111	7.0	93	5.4	99	3.1	100	2.8	104	12	110	7.6	124	3.6	119	4.3	120	6.4	117	11	108	6.1	83	6.3
Diflufenican	98	8.6	100	3.2	92	5.5	105	3.9	115	14	124	11	127	4.2	121	6.3	103	14	96	8.2	117	14	118	2.9

Diuron	115	6.4	101	1.8	100	9.1	99	2.4	97	12	100	3.4	96	4.9	89	2.2	85	5.0	83	5.9	97	2.3	87	3.4
Isoproturon	105	5.8	102	5.6	97	6.4	97	0.9	87	9.4	98	4.6	102	7.4	108	5.0	89	2.7	97	5.5	104	7.1	98	4.4
Chlortoluron	103	6.6	101	3.8	97	12	94	7.0	92	2.9	70	5.8	62	6.0	64	5.3	73	4.3	62	6.7	71	7.7	60	3.0
Flufenacet	107	5.4	97	9.6	100	4.8	99	0.9	103	4.4	92	4.1	98	7.3	119	4.6	92	14	81	12	97	6.5	117	4.3
Isoxaflutole	87	16	94	10	113	5.4	101	3.7	124	24	120	7.2	114	4.3	118	4.1	124	21	126	12	100	2.5	97	7.0
Mefenacet	105	6.0	98	3.9	104	3.2	99	1.7	111	2.8	87	5.7	86	7.2	111	4.3	84	3.3	63	5.6	67	6.1	82	5.6
Clodinafop-propargyl	107	5.7	98	2.2	111	8.3	90	10	76	6.8	62	1.4	30	3.3	58	9.4	76	9.2	44	3.5	20	3.5	41	4.9
Haloxyfop-r-methyl	107	7.0	94	8.4	95	7.2	99	4.1	106	1	86	11	82	5.8	110	5.9	86	9.7	65	6.6	78	9.0	87	7.0
Quizalofop-p-ethyl	113	8.4	101	3.4	95	7.9	103	3.8	119	6.3	100	5.8	100	10	114	2.6	104	12	74	8.7	91	9.4	94	9.4
Imazaquin	97	6.5	92	3.5	89	3.6	100	1.8	85	4.4	92	5.3	101	4.2	117	2.0	73	4.0	75	1.5	115	4.7	100	3.6
Imazethapyr	100	8.1	92	4.1	91	3.9	99	2.7	119	2.0	123	7.5	118	7.6	119	2.6	116	6.2	120	1.3	99	11	114	1.6
Butralin	106	18	127	16	102	8.8	94	8.3	114	15	81	8.7	72	3.7	71	3.1	94	19	81	18	70	14	92	18
Carfentrazone-ethyl	95	9.6	99	6.6	113	16	97	15	62	12	53	4.4	27	3.4	64	7.7	73	13	43	6	16	1.9	36	5.2
Pinoxaden	109	3.2	99	2.1	107	2.4	105	8.4	139	13	125	5.8	88	8.7	111	4.6	126	6.6	119	4.1	64	9.4	98	17
Fluazinam	111	7.1	95	8.1	92	9.1	103	8.8	118	5.6	98	6.6	118	9.0	86	5.5	104	16	84	16	100	18	85	13
Fluroxypyr	76	17	113	8.5	105	4.9	97	11	–	–	118	7.4	87	16	64	5.4	–	–	101	6.9	80	14	56	6.9
Metribuzin	102	2.6	102	1.9	100	2.4	98	2.4	91	11	83	3.6	79	2.7	85	2.1	111	5.8	110	5.2	85	7.2	75	0.8
Amicarbazone	103	8.0	87	3.4	90	2.1	100	1.3	122	2.0	126	8.3	108	3.7	124	3.5	81	5.2	79	2.8	77	3.6	63	4.7
Florasulam	101	9.7	94	5.1	101	8.6	105	1.0	102	10	97	4.5	98	4.0	79	2.6	96	6.0	91	5.7	99	4.6	72	2.6
Penoxsulam	101	8.7	91	3.8	85	2.4	103	3.5	120	5.6	125	17	116	7.5	129	0.7	84	2.4	83	2.9	80	5.2	93	11
Mesotrione	84	11	102	5.5	97	6.8	100	5.7	99	8.5	98	17	75	5.6	71	2.6	108	4.8	106	12	72	14	76	2.5
Fomesafen	115	1.4	104	2.1	111	6.9	93	7.0	127	21	125	12	97	7.2	112	6.3	99	12	103	9.3	84	12	109	5.8
Napropamide	108	6.3	104	5.2	95	5.8	98	1.2	110	9.1	91	8.1	94	6.5	101	3.0	93	5.3	72	7.2	75	8.6	83	4.7
Propyzamide	93	5.2	104	7.9	95	3.5	100	3.3	105	3.3	106	7.5	97	9.8	116	3.8	91	17	78	7.3	110	5.7	111	3.9
2,4-D	88	4.8	107	7.7	90	8.9	91	9.6	128	15	118	14	79	7.0	99	7.7	105	18	85	17	104	8.9	79	8.5
MCPA	90	11	98	6.7	91	9.7	93	8.6	104	13	87	11	84	5.6	110	5.7	102	15	84	5.6	110	12	108	12
Bentazone	112	7.7	108	2.7	101	7.5	97	3.5	83	16	85	5.9	87	3.1	89	3.3	115	5.0	109	6.0	89	7.3	114	4.8
Propham	94	9.7	104	5.0	94	2.0	94	3.0	111	5.5	105	3.5	100	5.0	101	3.6	97	8.7	86	5.9	78	4.9	73	4.0
Pendimethalin	95	7.7	96	6.9	86	3.7	104	4.5	110	11	96	9.9	117	8.2	113	4.0	83	15	74	14	108	18	124	11

Propoxur	92	5.6	104	2.9	96	2.1	101	2.4	89	3.5	108	2.2	95	2.7	91	1.4	101	6.4	115	2.7	103	6.3	96	6.5
Carbofuran	101	4.7	98	2.6	100	2.8	101	0.5	108	4.1	104	4.7	94	3.3	99	2.3	105	3.4	99	1.3	100	3.7	99	4.9
3-hydroxy- carbofuran	105	7.7	88	6.4	103	4.5	97	4.1	46	4.5	17	2.5	83	2.7	36	2.8	41	3.7	32	3.7	34	3.5	35	3.2
Aldicarb	94	14	95	14	99	8.9	104	11	21	2.6	18	2.4	50	2.6	92	7.2	88	11	91	7.5	95	9.6	112	18
Aldicarb-sulfone	105	9.2	87	4.3	104	7.0	104	4.6	118	2.4	109	1.7	88	6.6	103	3.6	93	1.8	84	3.3	99	9.7	80	4.4
Aldicarb- sulfoxide	106	8.8	99	8.7	97	8.1	114	7.0	122	3.6	121	7.1	106	8.4	106	11	104	14	88	12	82	17	74	6.3
Carbaryl	97	6.1	95	7.8	102	4.5	93	3.0	113	10	129	7.7	103	6.8	103	8.7	114	15	116	12	89	5.2	101	5.4
Diethofencarb	102	14	93	7.1	97	4.8	102	3.1	81	10	95	5.0	82	5.6	91	5.4	78	5.3	92	9.1	97	5.8	77	1.4
Fenobucarb	106	13	103	6.8	95	5.3	98	6.2	87	8.8	103	7.4	100	12	87	8.1	79	16	104	11	111	6.3	78	3.5
Indoxacarb	93	8.2	96	6.7	94	0.8	105	4.1	106	9.3	104	9.9	85	7.9	102	7.3	85	11	83	7.1	80	8.3	97	7.4
Isoprocarb	107	11	104	2.5	88	12	96	4.0	102	14	85	2.0	92	5.6	75	2.5	75	12	79	12	88	7.3	71	5.4
Methomyl	96	3.7	101	1.1	99	3.5	99	1.5	92	1.3	93	2.7	73	3.4	77	2.8	71	13	73	9.6	62	8.3	57	2.0
Pirimicarb	97	2.4	98	2.8	91	2.8	98	1.4	120	4.1	111	7.1	86	3.1	96	1.1	82	4.4	85	5.9	75	2.5	71	3.1
Acetamiprid	99	1.8	101	1.1	102	1.7	99	0.7	103	1.0	118	1.8	108	2.8	100	0.6	99	5.0	101	2.2	100	1.8	97	0.8
Clothianidin	90	8.3	114	6.2	96	5.7	94	4.4	99	4.7	81	11	89	4.3	72	3.6	104	7.1	108	15	129	9.2	104	9.7
Dinotefuran	109	11	85	6.5	103	8.0	116	6.7	83	3.3	92	2.0	108	15	101	6.8	77	8.3	72	6.5	109	12	77	8.6
Imidacloprid	106	4.1	99	1.7	103	4.8	100	1.8	103	7.6	115	6.2	102	5.3	109	3.8	103	7.6	105	15	112	5.6	114	11
Thiacloprid	98	4.4	108	2.8	103	2.6	97	2.4	99	3.8	105	2.2	108	1.4	110	2.2	132	3.9	141	5.0	137	3.5	128	6.2
Thiamethoxam	105	7.9	85	3.4	102	0.7	105	5.7	92	3.8	86	2.4	97	2.0	81	1.3	52	2.4	44	1.7	87	4.9	45	0.5
Diazinon	100	2.4	96	3.3	90	3.7	102	2.8	109	2.4	109	7.6	119	4.1	120	2.5	115	1.4	108	4.1	121	4.3	118	0.9
Profenofos	78	8	96	9.7	91	3.3	107	5.9	110	19	113	6.5	108	10	117	2.4	107	19	116	6.6	118	3.2	85	2.3
Dichlorvos	98	6.2	95	5.8	81	3.7	103	3.9	145	10	143	15	140	7.0	151	5.4	161	8.6	150	8.3	129	6.5	142	5.1
Dimethoate	101	2.5	94	3.2	98	1.8	95	5.1	51	2.4	49	0.6	54	0.3	42	5.0	79	4.6	75	5.0	88	5.9	111	11
Isofenphos- methyl	109	8.0	98	7.5	92	3.9	104	4.9	71	8	110	8.5	116	5.3	130	4.6	74	13	91	11	103	11	107	9.9
Malathion	92	11	96	5.8	98	11	97	3.0	111	7.5	109	6.7	107	3.3	117	4.7	113	16	104	7.4	90	2.9	108	7.4
Omethoate	99	4.3	101	1.9	98	0.8	100	1.0	99	2.2	99	0.5	91	1.9	98	1.2	98	6.5	98	3.4	90	2.0	90	0.7
Tolfenpyrad	118	17	91	6.4	82	6.1	110	11	–	–	99	7.0	115	2.0	84	6.5	–	–	86	12	106	17	86	5.6
Chlorobenzuron	94	19	94	4.0	105	7.6	102	3.5	73	13	71	15	73	7.7	99	2.7	91	18	94	12	98	1.8	114	3.3
Etoazole	98	14	92	5.6	90	6.4	104	7.2	149	8.8	141	12	129	4.8	109	5.3	113	12	128	7.1	111	14	111	7.2
Pyriproxyfen	106	8.9	105	5.8	92	3.8	104	3.9	99	5.1	119	7.2	95	4.0	96	5.4	72	12	89	5.2	90	13	91	11

Tebufenozide	109	7.1	100	4.7	99	4.3	101	4.9	104	8.5	103	8.2	98	9.4	92	5.0	102	10	104	11	117	6.7	95	4.3	
Cyproconazole	110	4.9	97	5.8	98	5.2	102	3.8	93	7.9	94	3.2	104	2.7	103	6.0	71	8.4	86	8.3	118	7.8	104	5.7	
Difenoconazole	112	10	99	4.6	97	7.8	102	3.5	110	7.5	82	7.8	112	8.4	89	5.8	96	7.4	78	4.8	125	15	92	6.0	
Diniconazole	112	4.1	94	5.1	103	4.9	102	3.4	76	3.9	80	4.7	100	5.4	89	4.8	99	4.8	108	3.2	125	2.9	108	7.1	
Epoxiconazole	98	3.6	95	6.6	95	4.5	103	3.2	122	3.0	118	7.0	119	5.0	129	5.5	110	3.2	99	3.9	106	7.1	94	3.9	
Flusilazole	104	4.4	95	5.4	98	3.1	104	2.5	103	2.6	98	1.2	98	4.3	102	7.9	104	11	100	3.4	99	4.0	103	7.2	
Myclobutanil	104	6.7	98	3.0	95	8.0	93	1.9	107	9.6	108	6.2	124	5.2	128	0.9	110	6.0	100	6.2	99	8.2	74	0.8	
Propiconazol	102	9.0	89	3.0	100	2.3	98	5.0	98	12	80	8.7	89	4.1	88	4.7	70	9.3	84	2.4	108	5.7	103	9.3	
Tebuconazole	102	6.9	99	3.7	95	2.6	104	2.9	106	2.9	105	4.1	102	6.3	104	5.7	112	3.7	111	10	116	5.1	95	7.2	
Triadimefon	103	4.7	95	3.4	102	5.4	99	4.3	113	3.7	104	3.6	107	4.4	103	7.4	110	4.2	108	6.1	112	3.9	92	4.5	
Triadimenol	99	5.5	95	2.7	98	2.4	99	4.0	107	8.5	114	3.2	95	3.5	87	5.2	80	6.9	96	8.0	108	6.4	85	6.0	
Triazophos	102	5.5	98	2.3	100	4.8	97	1.7	117	7.2	103	8.0	106	11	114	3.0	101	5.4	88	11	104	11	111	4.0	
Tricyclazole	108	4.6	83	2.4	98	4.9	105	7.0	80	15	91	8.3	88	5.9	78	3.5	79	5.4	83	8.7	103	5.6	72	3.2	
Azoxystrobin	102	11	95	2.5	97	3.2	103	3.4	98	2.6	98	2.9	96	8.4	99	6.8	92	5.8	93	4.5	92	3.8	75	2.5	
Fluoxastrobin	104	7.4	93	4.8	92	5.9	95	7.4	101	4.3	76	6.4	100	9.6	100	11	92	4.7	70	6.7	89	6.8	88	8.1	
Kresoxim-																									
methyl	99	9.3	75	4.7	89	17	98	3.0	83	4.7	80	4.5	73	3.1	86	4.9	101	2.4	60	3.4	54	1.9	68	2.9	
Picoxystrobin	108	11	97	3.5	98	6.2	101	3.9	87	3.1	77	6.3	89	6.1	92	5.5	93	6.5	86	11	104	10	97	7.7	
Pyraclostrobine	113	11	98	4.6	95	7.4	98	2.7	96	5.5	101	7.7	121	8.8	104	3.6	96	11	93	10	117	13	93	9.0	
Trifloxystrobin	96	4.2	100	3.5	99	3.4	101	1.8	120	2.5	111	4.2	134	4.5	141	6.6	102	9.3	84	7.2	109	7.4	118	9.2	
Prochloraz	105	4.7	104	5.4	97	4.5	98	2.9	127	7.0	128	4.9	118	12	103	5.3	123	8.1	129	4.9	108	11	79	4.8	
Triflumizole	106	6.6	93	3.7	97	3.7	105	4.2	97	6.8	96	3.9	102	4.0	96	5.6	97	4.9	93	4.8	103	6.4	88	5.3	
Imazalil	103	4.3	103	2.2	90	3.2	98	1.9	118	5.2	129	10	90	2.1	118	1.8	113	5.8	122	3.0	106	3.9	110	3.4	
Cyprodinil	109	13	103	5.3	105	7.5	98	3.9	70	8.9	101	4.7	102	2.9	88	4.3	83	6.8	102	9.8	98	6.6	88	2.5	
Pyrimethanil	106	13	98	5.7	95	2.0	98	4.4	99	8.8	96	5.3	93	4.8	85	2.8	112	5.8	110	12	116	7.5	90	1.1	
Carbendazim	101	1.0	101	0.4	99	0.8	100	0.5	118	3.4	104	3.6	98	2.6	106	0.6	105	5.1	111	1.8	110	0.8	107	0.2	
Thiophanate-																									
methyl	102	5.0	97	7.1	104	4.4	92	3.7	38	3.9	40	3.5	60	6.5	36	1.9	65	11	91	14	85	7.8	83	6.7	
Boscalid	107	7.4	102	2.6	102	4.1	91	5.4	122	5.0	85	7.4	87	8.0	103	9.7	102	7.7	76	6.0	89	7.2	93	5.4	
Dimethomorph	93	6.6	83	4.8	86	7.1	93	7.4	114	5.5	85	4.5	122	3.5	113	8.9	81	11	79	10	102	11	102	11	
Metalaxyl	108	12	97	2.9	98	5.5	99	4.9	111	7.5	116	2.8	96	4.7	100	5.4	81	4.1	96	12	80	4.5	74	5.8	
Oxathiapiprolin	108	6.3	96	5.0	110	5.7	97	5.6	128	7.5	113	5.9	104	7.3	119	3.5	99	5.6	75	11	66	5.9	72	4.3	
Isoprothiolane	101	2.7	95	10	98	3.8	92	1.3	104	5.0	96	8.9	99	8.0	108	1.8	83	4.7	73	11	90	7.2	107	3.7	

Table S9 Relative deviation of ion ratio of pesticides in spiked DW samples (%; n=5)

Chemical name	5 ng/L			25 ng/L			100 ng/L			1000 ng/L		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Paclobutrazol	-11	0	-4.8	-5.2	1.7	-2.2	-2.3	3.6	0.8	-2.7	3.5	0.2
Acetochlor	3.2	27	13	-15	2.7	-3.2	-13	11	-3.3	-9.3	8.5	0.6
Alachlor	-3.9	5.1	0.5	-8.4	9.4	1.1	-9.4	6.7	-0.6	-7.1	-1.9	-5
Butachlor	-22	-1.8	-11	-12	1.9	-2.5	6.4	12	9.5	-5.3	16	3.4
Metolachlor	-17	-2.7	-11	-5	19.1	7.4	-2	6.6	3.4	-5.0	3.0	-1.2
Pretilachlor	-5.2	3.6	-1.6	2.0	8.7	4.2	-8.8	-6.1	-7.4	5.7	11	8.1
Ametryn	-4.5	0.9	-2.5	-11	6.1	-2.5	-2.1	0.1	-0.9	0	0.9	0.2
Atrazine	-	-	-	-	-	-	-	-	-	-	-	-
Atrazine-desethyl	-3.4	3.4	0.4	-2.7	0.4	-1.4	-4.0	0	-1.8	-0.4	1.6	0.7
Atrazine-desisopropyl	-16	11	1.0	-12	2.9	-5.4	-3.7	3.4	0.8	-2.9	0.8	-1.5
Cyanazine	-5.8	16	8.1	-4.7	5.8	0.7	-6.9	3	-3.2	-5.2	-3.1	-4.4
Prometryn	-10	3.4	-3.9	-5.0	-1.0	-3.0	-6.7	-0.2	-3.4	-0.6	7.6	2.8
Simazine	-2.8	8.4	2.6	2.8	7.8	5	-6.1	5.8	2.7	5.9	7.5	6.5
Terbuthylazine	0	18	12	1.0	5.1	2.2	2.5	7.2	4.9	-2.0	6.1	1
Terbutryn	11	21	15	0.5	3.7	1.9	-1.6	0.1	-0.8	-7.0	1.4	-2
Bensulfuron-methyl	-3.5	11	4.6	-8	3.5	-2	-8.3	7.1	-0.7	0	7.9	2.1
Ethametsulfuron-methyl	-12	8.1	-1.2	5.4	22	16	-7.3	-3.0	-4.2	-2	4.9	-0.1
Nicosulfuron	3.5	14	8.4	1.5	9.7	5.6	-13	-5.9	-10	-0.6	1.2	0.4
Pyrazosulfuron-ethy	-15	16	3	0.5	3.4	2.2	-2.3	5.0	0.2	-3.3	0.5	-1.5
Tribenuron-methyl	-32	3.8	-11	0	6	3.4	-1.1	8.9	3.7	0	8.8	5.7
Diflufenican	-38	27	-4.5	-19	7.9	-7.1	-12	13	0.6	-1.2	6.7	3.3
Diuron	-26	18	-3.5	-13	-3.6	-8.9	-12	-0.6	-4.5	-3.8	5.7	-0.8
Isoproturon	-17	0.3	-12	-6.6	1.3	-3.9	-12	6.8	-3.2	-0.3	2.0	0.9
Chlortoluron	-6.7	13	3.3	-4.9	8.2	2.6	-10	-2.9	-6.9	-3.1	0	-1.6
Flufenacet	-14	-3.3	-8.3	5.1	9.9	6.9	-1.2	5.9	2.1	-4.4	2.8	-0.9
Isoxaflutole	-	-	-	-	-	-	-	-	-	-	-	-
Mefenacet	0.3	8.7	5.4	-4.9	4.0	-2.0	3.9	16	9.3	-2.5	0.9	-0.8
Clodinafop-propargyl	-22	-3.0	-15	-3.7	14	5.5	-13	-2.3	-7.1	-1.7	2.6	0.5
Haloxypop-r-methyl*	-	-	-	-7.1	21	11	-23	11	-7.4	-3.4	10	4.1
Quizalofop-p-ethyl	-23	-4.0	-15	-1.6	8.3	3.9	-9.0	-2.0	-5.4	-4.0	1.5	-0.4

Imazaquin	-1.8	5.2	2.8	-6.9	2.1	-2.1	-1.7	3.4	1.7	-2.2	0.3	-0.6
Imazethapyr	-0.5	3.9	1.2	-2.9	1.2	-0.9	-1.0	2.1	0.3	1.7	2.7	2.2
Butralin	-13	13	2.2	11	25	17	-22	-14	-19	-4.2	6.9	-0.7
Carfentrazone-ethyl	-8.9	22	15	-7.6	12	2.5	-20	-3.1	-13	-12	7.8	-2.7
Pinoxaden	-12	3.6	-1.2	-6.1	9.8	2.4	-5.5	11	5.1	-17	1.2	-6.9
Fluazinam	-4.5	2.9	-1.5	-5.1	5.5	-0.7	-3.8	14	5.6	-1.8	-0.4	-0.9
Fluroxypyr	-24	18	-5.3	-3.0	18	5.7	-1.8	7.3	2.0	-18	-11	-14
Metribuzin	0	25	5.5	-15	7.5	-4	-21	-11	-17	-2.8	0	-1.7
Amicarbazone	-12	0	-7.9	4.3	8.5	6.4	-3.6	3.1	-0.9	0	0	0
Florasulam	-30	16	-14	3.8	15	9.6	-7.8	-2.6	-5.2	-6.6	-3.3	-5.2
Penoxsulam	-11	10	0.2	-12	-3.4	-6.7	-2.1	4.4	0.5	-2.3	0.5	-0.6
Mesotrione	-15	30	6.5	-21	21.7	-0.1	-3.0	14	2.7	-11	-2.9	-6.5
Fomesafen	-22	-5.8	-12	-14	-8.2	-11	-7.7	9.3	0.3	0.1	5.7	3.6
Napropamide	-8.0	1.8	-3.0	-8.9	0.3	-4.0	-3.7	5.1	0.7	-1.8	0.1	-0.4
Propyzamide	-7.5	27	10	-4.0	7.7	0	-19	6.4	-1.9	-2.9	2.9	-0.6
2,4-D	-	-	-	-	-	-	-	-	-	-	-	-
MCPA*	-	-	-	-20	20	1.0	-22	22	-4.4	-5	20	6.0
Bentazone	-13	3.6	-5.6	2.7	14	8.2	-2.9	3.4	1.9	-4.8	0.9	-2.0
Propham	-15	23	5.1	-11	13	-1.0	-16	-2.5	-7.9	0.4	4.8	2.0
Pendimethalin*	-	-	-	-18	-3.4	-11	-9.7	8.1	-1.3	-3.1	7.6	0.9
Propoxur	3.1	6.5	5.3	-1.6	4.9	1.0	-0.4	6.5	2.9	-2.3	-0.5	-1.4
Carbofuran	-6.3	4.7	0.3	-4.2	2.4	-0.8	-8.2	-0.8	-5.6	-1.2	3.5	1.7
3-hydroxy-carbofuran	-2.8	-1.1	-1.8	-3.1	-1.1	-2.1	-2.7	0	-0.8	-3.5	-0.9	-2.3
Aldicarb	-2.0	8.6	2.7	-2.1	0.8	-0.3	-2.3	1.1	-1.3	-0.4	2.0	0.8
Aldicarb-sulfone	-17	0	-9.1	-5.9	1.4	-2.5	-6.4	-3.1	-5.0	-26	-12	-18
Aldicarb-sulfoxide	-6.9	20	3.2	-0.9	2.6	0.7	-3.0	-1.1	-2.0	-2.2	-0.9	-1.4
Carbaryl	-3.3	21	7.7	-4.7	5.4	0.7	-0.6	9.5	2.9	-0.9	3.7	2.0
Diethofencarb	-8.3	2.8	-3.3	-1.2	6.9	3.8	-1.8	4.1	0.9	-7.8	-1.6	-4.5
Fenobucarb	-3.3	19	6.2	-23	-1.2	-10.6	-12	-3.3	-7.9	-18	0.6	-7.6
Indoxacarb	10	23	18	-10	28	11	-0.5	9.6	4.1	5.2	12.9	10.7
Isoprocarb	-11	-1.3	-7.1	-18	-10	-14	-6.8	-0.1	-2.9	-7.4	3.5	-1.6
Methomyl	0.2	4.2	1.8	-3.3	-1.3	-2.3	-1.2	0.9	0	-0.3	0.7	0.2
Pirimicarb	-2.0	0.5	-0.5	-0.2	1.1	0.5	-0.7	0.1	-0.4	0.2	0.8	0.5

Acetamiprid	-2.5	2.9	-0.4	-0.4	1.9	0.4	-3.6	0.4	-1.0	-3.5	0.2	-1.8
Clothianidin	-3.6	7.8	1.9	2.9	9.1	5.4	1.1	4.1	2.4	-2.0	0.2	-0.5
Dinotefuran	-8.5	18	5.6	-3.4	3.4	0	2.4	9.0	5.1	-0.9	3.4	0.8
Imidacloprid	-9.7	-6.4	-8.4	-0.7	4.2	1.0	-2.8	20	-0.3	0.5	1.0	0.8
Thiacloprid	-2.9	5.9	2.6	-7.4	1.2	-2.1	-2.1	5	1.7	-2.5	0.8	-0.6
Thiamethoxam	-0.4	1.9	0.7	-0.4	2.5	0.8	-2.7	-0.9	-2.1	-1.9	0.6	-0.4
Diazinon	-5.5	-0.9	-3.3	-1.1	2.3	0.4	-6.4	-1.3	-3.1	-4.5	1.4	0
Profenofos*	-	-	-	-	-	-	-23	-7.7	-13	-7.7	23	11
Dichlorvos	-21	10	0.2	-20	-5.3	-12	-4	10	3.9	-4.3	4.3	-0.6
Dimethoate	1.9	7.8	4.1	-1.0	-0.2	-0.5	-3.4	0	-0.9	-7.3	-6.1	-6.6
Isofenphos-methyl	5.0	15	9.5	-8.2	9.5	2.6	-11	1.0	-3	-9.5	1.8	-1.4
Malathion	-1.0	22	12	-0.1	15	7.7	-4.8	21	10	-3.8	5.3	2.6
Omethoate	-1.8	5.6	2.7	-4.5	0.6	-1.2	0.8	3.0	1.9	-2.2	0.6	-0.7
Tolfenpyrad	-27	12	-2.3	-20	17	-2.4	-18	5.8	-2.3	-6.8	1.6	-1.9
Chlorobenzuron*	-	-	-	-35	27	-0.4	-18	15.6	-4.7	-14	11	0.2
Etoazole	-0.4	9.8	4.4	0.4	2.2	1.2	-1.9	0.9	-0.5	5.2	11	6.9
Pyriproxyfen	2.2	11	5.9	-2.3	1.1	-1.2	-1.7	9.6	1.8	-2.1	2.4	0.5
Tebufenozide	-1.8	5.0	2.6	-2.4	-0.9	-1.4	-0.8	2.0	0.8	-2.2	0.6	-0.6
Cyproconazole	-6.5	13	3.8	-2.9	4.5	-0.1	-5.6	2.8	-1.9	-5.1	-2.9	-3.8
Difenoconazole	-15	19	-1.9	-2.9	1.1	-1.4	-5.4	0.9	-2	-4.5	0.6	-0.9
Diniconazole	-7.7	9.2	1.2	6.6	15	10	-21	-7.9	-12	-11	-5.7	-8.9
Epoxiconazole	-17	14	0.6	0	15	5.8	-2.1	9.7	3.9	-5.5	0.5	-1.6
Flusilazole	-5.7	4.2	-2.7	-4.2	2.2	-0.2	-2.9	12	2.8	-11	3.3	-3
Myclobutanil	0.9	13	6.5	-5.8	4.1	-3.1	1.2	5.2	2.8	3.4	5.6	4.5
Propiconazol	-1.7	15	9.3	-9.8	11	2.6	-8.9	6.1	1.2	1.6	3.2	2.1
Tebuconazole	-30	21	-10	-22	3.7	-5.4	-12	5.2	-4.9	-16	10	-5.2
Triadimefon	-12	2.8	-5.1	-4.9	10	2.3	-6.6	9.8	0.5	-2.6	0.7	-0.5
Triadimenol	-10	28	7.6	-9.1	6.1	-2.4	2.9	8.1	5.8	-6.1	0	-3.6
Triazophos	0.8	16	9.1	-0.7	13	6.9	-1.8	4.7	0.4	-1.8	3.3	0.7
Tricyclazole	-1.2	12	4.0	0.5	4.9	2.3	-0.5	2.9	1.4	0	0.6	0.4
Azoxystrobin	-9	6.7	-2.4	-2.4	-0.3	-1.1	-6.1	4.5	-0.5	-4.3	0	-1.8
Fluoxastrobin	-14	10	-1.2	7.6	11	9.9	-5.3	3.0	-0.5	-4.4	0.7	-1.3
Kresoxim-methyl	-22	-2.5	-9.1	2.5	10	6.0	6.4	11	7.7	-3.9	1.8	-1.2

Picoxystrobin	-8.8	3.4	-0.8	-1.0	2.4	0.8	1.2	2.5	1.9	-2.8	1.8	-0.3
Pyraclostrobine	-2.4	2.4	1.0	4.4	10	6.7	-3.1	2.6	0.6	-1.3	3.3	1.4
Trifloxystrobin	-8.2	7.2	0.7	-6.2	3.0	-2.5	-10	-2.3	-6	2.9	6.8	4.4
Prochloraz	-14	27	-2.5	-17	14	1	3.6	17	8.8	-8.7	5.7	0.6
Triflumizole	-4.4	4.8	0	2.4	5.3	4.1	-1.7	6.3	1.9	-3.2	-0.4	-2.1
Imazalil	-11	-3.9	-7.7	-6.1	2.2	-1.3	-2.2	2.8	1.1	-1.6	1.1	-0.4
Cyprodinil	-9.9	5.5	-2.0	-2.8	6.0	1.5	-5.5	0.9	-2.1	0.5	1.8	1.4
Pyrimethanil	-7.2	12	-2.0	-3.3	4.8	1.2	2.1	6.6	4.3	0.4	2.5	1.1
Carbendazim	-4.2	-0.5	-2.0	-1.4	-0.5	-0.9	-0.7	0.7	-0.1	0.5	0.5	0.5
Thiophanate-methyl	-28	3.9	-6.3	-19	-3.9	-8.6	-2.7	6.1	2	7.8	13	9.4
Boscalid	7.3	17	13	-4.0	9.7	1.7	1.8	15	8.1	-2.8	11	4.3
Dimethomorph	-15	9.7	1.9	-18	-9	-12	-4.4	9.6	0.6	-6.6	1.4	-1.9
Metalaxyl	-8.3	1.2	-4.7	-1.3	6.2	2.8	-6.5	1.7	-3.1	-3.1	0.9	-1.2
Oxathiapiprolin	-12	24	4.3	-3.6	7.5	1.9	-8.8	7.8	-0.3	-16	12	1.0
Isoprothiolane	-7.9	12	-0.4	-1.9	0.4	-0.6	-2.0	0.3	-0.7	4.2	8.5	6.4

* means that the pesticide with defect in the calculation of relative deviation of ion ratio at low or low-medium concentration due to insufficient response of confirmation ion compared to quantitative ion.

Table S10 Relative deviation of ion ratio of pesticides in spiked SW samples (%; n=5)

Chemical name	5 ng/L			25 ng/L			100 ng/L			1000 ng/L		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Paclobutrazol	-8.3	14	1.3	-8.6	11	1.4	0.3	7.5	2.6	0	26	7.3
Acetochlor*	-	-	-	-9.2	12	2.8	-16	5.2	-5.8	-16	12	-0.2
Alachlor	-6.6	1.2	-2.7	5.1	21	13.5	-17	-3	-7.8	-14	-4.2	-9.1
Butachlor	-16	-4.1	-12	-9.7	14	-3.5	-8.7	11	-0.8	1.3	15	10
Metolachlor	-6.9	7.7	-2.3	-0.3	26	12	-6.7	12.4	4.4	5.9	15	9.6
Pretilachlor	-0.8	7.4	3.1	2.2	8.4	4.5	-12	6.2	-5.6	4.2	12	7
Ametryn	-0.9	16	9.7	0	9.6	6.1	-4	-0.2	-1.9	-2.8	2.8	-0.2
Atrazine	-	-	-	-	-	-	-	-	-	-	-	-
Atrazine-desethyl	-14	0	-4.7	-12	-7.6	-10	-4.9	4.9	-1.3	-0.4	3.6	1.6
Atrazine-desisopropyl	0.1	14	7.3	-10	14	2.3	-7.1	-0.7	-3	4.5	13	9.5
Cyanazine	-10	9.3	-1.4	5.8	11.6	8.4	0.6	11	4.7	-3.1	2.1	-0.2
Prometryn	6.5	25	17	4.9	9.8	6.9	-3.4	0.1	-1.6	15	25	18
Simazine	-6.0	14	1.1	-3.5	12	2.4	1.4	6.7	3.2	2.4	9.3	5.7
Terbuthylazine	10	24	16	1.0	10	6.5	1.2	8.2	5.3	2.0	9.2	5.9
Terbutryn	-28	-22	-26	-14	-8.4	-11	-8.1	-0.1	-2.9	8.2	15	11
Bensulfuron-methyl	0.2	15	8.3	1.2	7.8	4.4	-8.0	3.3	-4.4	11	16	15
Ethametsulfuron-methyl	-21	3.3	-11	-5.0	5.4	0	-18	-11	-15	-24	-20	-22
Nicosulfuron	0.9	9.8	6.4	1.9	6.4	3.7	-16	-8.7	-12	-1.0	2.2	0.2
Pyrazosulfuron-ethy	-13	12	-2	1.5	12	6.2	-10	16	1.6	-2.4	2.4	-0.2
Tribenuron-methyl	-22	-12	-18	-6.0	11	0.9	-5.6	8.5	-1.5	8.8	15	11
Diflufenican	-29	13	-11	-12	26	5.4	7.1	19	14	0	15	9.3
Diuron	-19	8.8	-5.6	-29	21	-2.5	-4.6	15	5.5	-7.5	1.9	-3
Isoproturon	-14	-1.4	-6.4	7.3	19.1	13.5	-9	8.8	0.9	0	5.0	2.1
Chlortoluron	-12	23	8.0	-1.6	13	6.2	-11	3.0	-6.3	-4.7	0	-1.6
Flufenacet	-12	4.0	-2.7	-0.8	11	5.4	-6.6	4.7	0.1	-1.4	5.1	2.7
Isoxaflutole	-	-	-	-	-	-	-	-	-	-	-	-
Mefenacet	-1.9	24	9.4	-8.6	1.5	-3.0	5.3	11	8.9	-2.8	7.3	2.9
Clodinafop-propargyl	-13	12	-4.2	5.5	21	15	-15	4.4	-5.4	-3.5	1.7	-0.3
Haloxypop-r-methyl*	-	-	-	7.1	-	-	-17	20	-5.1	-21	10	-1.4
Quizalofop-p-ethyl	1.8	23	11	-13	3.6	-2.1	-3.6	2.6	-0.5	-3.5	1.5	-1.2

Imazaquin	2.0	12	7.2	-7.2	-1.6	-3.6	-2.9	0	-1.5	-3.2	2.7	-0.2
Imazethapyr	1.4	5.8	2.9	0.2	4.8	3	-1.8	11	2	7.1	11	8.4
Butralin	-24	13	-8.7	-13	2.9	-3.4	-29	-13	-19	-3.3	1	-1.9
Carfentrazone-ethyl*	-	-	-	-13	14	0.3	-21	22.6	-6.7	-20	5.1	-7.6
Pinoxaden	-4.8	25	15	13	20	17	-1.5	16	8	-26	24	-1.9
Fluazinam	-11	-3.8	-7.5	-4.6	5.1	-0.8	7.4	20	16	-2.9	1.6	-1.6
Fluroxypyr*	-	-	-	-	-	-	-5.8	14	2.2	-23	-16	-20
Metribuzin*	-	-	-	-	-	-	-30	-27	-29	-17	-8.3	-12
Amicarbazone	-2.9	13	2.9	4.3	13	8.9	-6.3	-1.1	-4.6	-2.2	2.2	0
Florasulam	-7.1	8.9	-2.1	-1.9	27	11	-2.8	9.4	2.7	-8.2	0	-5.2
Penoxsulam	2.2	25	15	-7.3	-4.3	-5.7	4.9	12	9.3	6.8	12	8.6
Mesotrione*	-	-	-	5.0	26	15	-11	20	2.7	-14	-7.7	-9.9
Fomesafen	-14	3.2	-6.9	-18	16	3.1	-18	-2.1	-9	2.6	17	8.6
Napropamide	-15	3.9	-8.7	-6.8	5.2	-1.3	-7.1	2.1	-1.5	-3.1	4.8	-0.2
Propyzamide	-12	56	17	-15	14	0.7	-4.6	5.4	1.8	-3.4	6.4	-0.3
2,4-D	-	-	-	-	-	-	-	-	-	-	-	-
MCPA*	-	-	-	-5.0	30	15	-11	22	8.9	-5.0	0	-2.0
Bentazone	-11	-2.6	-6.8	1.1	17	7.8	-7.4	8.7	0	-5.7	-1	-3.6
Propham	-3.5	12	5.4	-7.9	27	7.9	-17	-2.8	-8.8	1	9.6	3.4
Pendimethalin*	-	-	-	-24	5.4	-6.4	-8.7	19	6.6	-0.8	6.1	2.0
Propoxur	0.1	6.4	3.7	-0.3	4.3	1.4	1.6	8.6	4.6	-1.2	4.7	0.6
Carbofuran	-14	7.7	-2.5	-6.2	3.6	-2.0	-11	1	-5.3	2.4	3.9	3.1
3-hydroxy-carbofuran	-0.6	28	12	-19	10	-3.0	-1.8	3.4	0.5	-4.2	-2.0	-3.0
Aldicarb	4.4	19	13	-5.8	1.5	-1.6	-3.9	0.8	-2.6	-0.6	0.8	0
Aldicarb-sulfone	-27	12	-5.6	-13	11	2.5	-10	3.8	-4.8	-31	-23	-26
Aldicarb-sulfoxide	6.9	22	15	-1.5	12	4.0	-4.0	-2.3	-3.2	-0.4	8.7	2.5
Carbaryl	2.4	15	8.8	-0.4	23	9.7	-2.6	10	3.2	-5.1	7.5	2.1
Diethofencarb	-22	-8.2	-17	-9.1	14	0	-12	9.5	-0.9	-6.8	-3.6	-5.1
Fenobucarb	-21	18	1.9	-11.6	5.8	-2.4	-9.2	8.8	-3.2	-12	-5.3	-9.6
Indoxacarb	-12	11	1.8	-13	19	8.9	-4.5	7.7	-0.5	-4.5	14	6.1
Isoprocacb	-37	-3.3	-21	-17	-6.0	-11	-16	-3.8	-8.7	-11	1.4	-3.8
Methomyl	-2.4	4.4	1.3	-4.1	-1.3	-2.0	-1.2	1.8	0.3	-1.7	0.3	-0.8
Pirimicarb	-9.4	-6.9	-8.3	-3.3	-1.7	-2.6	-2.1	0	-0.9	2.0	2.8	2.3

Acetamiprid	-12	18	1.2	3.8	8.4	6.9	-14	-8.7	-11	-2.0	0.2	-1.1
Clothianidin	-2.0	18	4.4	-14	7.9	-5.1	-1.5	7.1	2.3	-4.3	-2.2	-3.2
Dinotefuran*	-	-	-	9.4	19	15	4.2	13	8.9	-0.2	2.3	0.8
Imidacloprid	-11	14	2.3	11	24	15	1.5	12	8.9	-1.5	11	5
Thiacloprid	-11	7.1	0.8	-4.5	0	-2.9	-2.1	4.5	1.3	-2.5	2.1	-0.1
Thiamethoxam	-15	4.6	-6.1	-3.5	2.9	-1.6	-2.2	-0.9	-1.7	-2.1	-0.4	-1
Diazinon	0.6	3.9	2.2	0.6	6.7	3.2	-2.8	3.2	-0.2	3.5	11	8.2
Profenofos*	-	-	-	-	-	-	-15	23	6.2	0	15	9.2
Dichlorvos*	-	-	-	2.1	24	16	9.9	23	16	4.3	18	14
Dimethoate	8.7	17	14	1.1	5.9	3.2	-1.3	2.4	-0.1	-7.3	-5.4	-6.4
Isofenphos-methyl	-17	29	14	-4.4	14	5.2	-3.4	5.2	1.8	8.9	21	16
Malathion	-8.5	26	2.8	5.1	19	13	1	24	14	-14	-7.2	-9.8
Omethoate	-2.7	10	2.2	0	2.7	1.8	-1.9	4.3	0.8	-1.4	2.2	0.5
Tolfenpyrad	-18	11.5	-7.6	-19	2.6	-7.3	-8.3	5.5	-0.3	-7.8	6.8	-2.3
Chlorobenzuron*	-	-	-	-	-	-	-21	7.5	-10.5	-9.8	-3.3	-6.7
Etoxazole	13	26	18	9.8	16	13	-2.9	0.1	-1.7	8.1	23	17
Pyriproxyfen	-1.5	8.3	2.4	0.3	5.7	2.7	-0.7	2.7	1.5	0.6	3.6	1.8
Tebufozide	2.8	23	8.8	-17	10	-0.6	0.1	13	5.4	-0.6	1.9	0.7
Cyproconazole	-8.2	15	4.1	-6.1	-0.5	-3.5	-5.8	6.7	0.9	-4.8	0	-2.3
Difenoconazole	-13	1.1	-4.5	-7.5	5.2	-1	-4.6	3.8	0.7	-2.8	-0.6	-1.6
Diniconazole	-12	17	0.6	-1.6	28	9.5	-6.7	9.8	-0.5	-7.1	-4.3	-5.7
Epoxiconazole	3.1	14	9.3	-5.2	19	4.9	1.3	20	8.1	8.2	15	13
Flusilazole	-14	4.6	-4.2	-4.9	3.3	-0.6	0.9	14	7.6	-2.2	7.1	0.9
Myclobutanil	-0.6	12	2.9	-9.0	10	2.4	-17	6.4	-2.9	9.9	19	14
Propiconazol	-1.7	29	13	-12	1.5	-6.6	-4.9	2.7	-1.1	-0.8	9.6	4.2
Tebuconazole	-10	-0.9	-6.6	-18	9.7	-6.3	-12	16	-1.3	-11.9	-1.4	-7.6
Triadimefon	-4.8	9.8	4.1	-2.2	11	3.3	0.4	5.4	2	-6.5	1.0	-2.8
Triadimenol	-21	3.4	-6.2	-9.1	0	-4.8	-0.4	11	5.8	3	12	4.8
Triazophos	17	26	20	2.2	11	5.1	-7.0	2.2	-3.1	7.6	14	11
Tricyclazole	-1.6	7.4	3.2	-3.0	5.8	2.4	0.5	3.3	1.7	0.1	2.0	0.9
Azoxystrobin	-3.5	2	-1.9	-2.1	1.5	-0.2	-2.9	1.2	-0.9	-4.0	1.8	-0.7
Fluoxastrobin	-23	6.4	-3.9	-4.4	18	6.9	-8.5	4.3	-0.5	-1.5	3.7	0.7
Kresoxim-methyl	-16	19	-1.7	5.4	22	12	0.8	7.2	4.9	-2.4	0.4	-0.4

Picoxystrobin	-2.9	0.8	-1.5	-5.8	7.5	0.1	-5	3.1	0.8	-0.5	3.7	1.2
Pyraclostrobine	0	5.1	2.7	4.3	9.9	7.7	-6.5	-1.0	-2.6	15	22	18
Trifloxystrobin	-7.2	8.4	1.8	-3.5	-0.7	-2.0	3.6	6.6	4.7	8.4	14	9.7
Prochloraz	-2.8	27	14	16	30	22	1.5	20	13.2	-2.5	11	2.9
Triflumizole	-18	10	-6	-8.5	6.5	-0.2	-5.1	4.2	-0.7	-2.8	-0.4	-1.6
Imazalil	0.6	17	5.1	2.0	7.7	4.4	-5.3	9.3	1.1	6.0	7.1	6.7
Cyprodinil	-9.9	17	2.9	-13	3.5	-5.3	-1.8	1.2	-0.2	1.1	3.3	1.8
Pyrimethanil	-9.1	3.5	-0.6	-5.8	11	5.1	1.3	9.8	4.2	-9.3	1.1	-3.4
Carbendazim	-2.8	-0.5	-1.7	-0.5	0.5	-0.1	-0.7	0.4	-0.2	-0.5	1.0	0.5
Thiophanate-methyl	-25	-1.3	-15	-29	-5.2	-17	-12	3.3	-3.8	1.6	16	8.4
Boscalid	-4.6	27	5.2	-16	9.7	-2.9	-6.1	23	11	-1.4	6.9	2.5
Dimethomorph	-2.7	21	13	-20	-10	-15	-3.1	4.2	-0.1	0.5	23	11
Metalaxyl	-1.3	7.6	3.6	7.2	18	13	-11	0	-5.2	-2.4	-0.9	-1.6
Oxathiapiprolin	15	29	23	0.8	29	19	-5.8	8.5	0.6	4.8	18	11
Isoprothiolane	0.2	9.0	6.2	2.2	7.5	5.0	-4.1	0	-2.2	17	24	21

* means that the pesticide with defect in the calculation of relative deviation of ion ratio at low or low-medium concentration due to insufficient response of qualitative ion.

Table S11 Relative deviation of ion ratio of pesticides in spiked WWE samples (%; n=5)

Chemical name	5 ng/L			25 ng/L			100 ng/L			1000 ng/L		
	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean	Min.	Max.	Mean
Paclobutrazol	-11	23	1.5	-10	-0.9	-7.6	-2.0	4.5	1.3	0.9	6.2	4.2
Acetochlor*	-	-	-	-7.7	8.5	4.5	-16	2.9	-8.8	3.0	6.4	4.0
Alachlor	-18	8.9	-4	-19	21	2.8	-9.1	9.5	0.8	-13	-4.9	-7.8
Butachlor	-28	1.2	-9.9	-9.7	1.9	-3.1	-21	25	3.5	-23	-2.6	-8.7
Metolachlor	-12	5.8	-6	-0.3	20	11	-2.2	21	6.9	4.4	17	11
Pretilachlor	-17	7.7	-0.1	-18	8.7	0.2	-9.1	-2.7	-6.3	2.8	7.4	5
Ametryn	0	4.5	2.0	0	8.8	4.2	-4.3	-0.9	-2.8	-1.8	0.9	0
Atrazine	-	-	-	-	-	-	-	-	-	-	-	-
Atrazine-desethyl	-9.6	22	7.3	-0.8	2.3	0.7	-0.3	1.6	0.8	2.0	4.4	3
Atrazine-desisopropyl	-24	12	-7.1	-11	9.5	-0.6	-5.6	4.9	-1.1	-4.3	2.0	-0.2
Cyanazine	-2.3	27	13	2.3	12.8	5.3	5.0	18	11	-5.2	2.1	-1
Prometryn	-1.4	11	3.5	-0.7	9.0	4.3	-4.1	0.3	-1.8	4.2	7.3	5.5
Simazine	-8.3	13	1.2	1.5	8.1	3.6	1.0	8.2	5.0	4.3	7.8	5.9
Terbuthylazine	6.7	20	13	-2.0	8.1	2.4	4.6	13	8.9	0	4.1	2.2
Terbutryn	3.2	15	9.2	-5.7	2.5	-1.7	-7.9	-3.5	-5	-5.9	4.3	-1.6
Bensulfuron-methyl	-17	7.5	-1.3	-7.4	7.5	-1.9	-10	3.9	-2.4	-2.6	7.9	3.2
Ethametsulfuron-methyl	4.4	21	15	13	20	18	-15	-6.9	-10.2	-4.6	4.6	-0.8
Nicosulfuron	-2.4	15	7.7	1.1	6.4	3.6	-13	0.6	-5.9	-4.7	0.6	-2.3
Pyrazosulfuron-ethy	-8.9	27	7.2	-2.5	15	3.6	-6.1	-2.1	-4	-7.7	-1.0	-3.8
Tribenuron-methyl	-18	0.8	-7.8	-8.5	10	4.1	-11	2.3	-5.2	-4.9	2.0	-0.8
Diflufenican	-21	0.6	-7.9	-23	10	-1.2	-4.4	27	11	3.6	22	10
Diuron*	-	-	-	-11	14	-0.7	-11	21	6.4	-1.9	7.5	2.3
Isoproturon	-28	-8.5	-19	-7.3	22	3.8	-10	0.4	-5.1	-2	4.7	1.1
Chlortoluron	-25	10	-14	-4.9	4.9	-0.3	-8.7	6.7	-1.3	-3.1	1.6	0
Flufenacet	-30	20	-5.0	2.0	13	7.1	-12	5.5	-0.2	2.8	6.1	4.6
Isoxaflutole	-	-	-	-	-	-	-	-	-	-	-	-
Mefenacet	-5.5	7.1	-0.5	-13	-0.3	-6.3	5.2	12	7.8	-8.9	1.3	-2.2
Clodinafop-propargyl	-25	21	0.7	-11	25	2.8	-9.4	8.8	-0.3	-12	10	-0.2
Haloxypop-r-methyl*	-	-	-	-	-	-	-29	11	-5.1	-17	-3.4	-12
Quizalofop-p-ethyl	-34	14	-7.3	1.6	16	8.4	-4.1	1.4	-1.1	-7.5	0.5	-2.6

Imazaquin	-5	9.5	3.8	-5	-1.1	-2.4	-3.9	0.4	-1.8	-1.7	0.2	-0.5
Imazethapyr	-1	11	6.2	-3.3	4.3	0.4	-0.6	21	4.5	1.2	12	6.5
Butralin	-24	13	-0.8	9.6	24	16	-18	-4.3	-13	0	1.6	0.5
Carfentrazone-ethyl*	-	-	-	-22	6.8	-5.5	-16	16	-0.5	-23	8.3	-0.7
Pinoxaden	-14	23	12	1.2	23	12	-10	4.4	-1.4	-8.3	8.3	1.9
Fluazinam	-11	20	1.1	-1.8	2.9	0.7	0.4	11	5.8	-2.9	0.5	-0.9
Fluroxypyr*	-	-	-	-	-	-	-21	21	1.8	-19	-16	-17
Metribuzin*	-	-	-	-	-	-	-29	-1.2	-20	-17	-5.6	-11
Amicarbazone	-28	4.4	-12	-2.1	11	6.4	-6.3	-1.8	-3.9	-6.5	4.3	1.7
Florasulam	-18	18	5	0	17	8.1	-4.4	5.6	0.5	-8.2	-3.3	-6.6
Penoxsulam	-25	-2.6	-16	-16	1.7	-6.6	-10	-0.9	-4.7	-1.4	6.4	1.8
Mesotrione*	-	-	-	-8.9	20	7	-8.6	15	4.2	-9.1	-5.3	-6.5
Fomesafen	-45	13	-17	-33	3.0	-11	-13	6.6	-7.3	3.6	9.3	6.2
Napropamide	-8.5	1.5	-4.9	-9.1	2.3	-2.6	-9.8	3.2	-1.9	-2	0.4	-0.9
Propyzamide	-14	37	0.9	-6.1	41	7.4	-8.2	7.8	2.1	-3.4	7.1	2.6
2,4-D	-	-	-	-	-	-	-	-	-	-	-	-
MCPA*	-	-	-	0	15	6	-28	39	-1.1	-15	30	4
Bentazone	-23	12	-3.1	8.8	24	18	-4.6	0.7	-1.6	1.7	23	10
Propham	-26	17	-13	-7.1	17	0	-18	9.7	-7.3	-0.6	10	4.8
Pendimethalin*	-	-	-	-14	12	-2.9	-9.2	0.3	-5.8	5.3	20	11.5
Propoxur	-3.1	7.9	1.9	-4.2	7.1	0.5	2.4	10	5.4	-0.9	2.9	0.5
Carbofuran	-4.3	8.6	0.4	-3.9	9.1	3.4	-10	-1.6	-6.7	1.8	7.2	4.3
3-hydroxy-carbofuran	-25	-16	-21	-23	-8.6	-17	-7.9	11	4.1	-5.8	-0.7	-1.9
Aldicarb	-11	13.8	4.5	-2.9	4.1	0.7	-4.8	2.5	-1	-3	2	-0.3
Aldicarb-sulfone	-18	9.6	-4.5	-11	0.9	-4.8	-7	-0.8	-3.7	-29	-21	-26
Aldicarb-sulfoxide	-6.3	23	5.1	-1.3	5.3	1.5	-7.6	-2.8	-5	-3	1.3	-0.3
Carbaryl	3.6	16	11	-11	11	-0.5	-10	21	1.7	-1.9	5.6	1.5
Diethofencarb	-24	-6.2	-12	-3.3	18	4.8	-2.3	3.1	1.1	-9.2	-1.1	-5.3
Fenobucarb	-8.6	22	6.9	-23	3.5	-11	-4.9	8.5	-0.2	-10	-3.5	-7.3
Indoxacarb	-12	28	13	-11	11	4.7	-23	4.9	-9.9	-0.2	13	7.2
Isoprocacb	-34	14	-11	-15	5.2	-5.4	-6.8	7.3	-2.2	-13	-6.8	-8.6
Methomyl	-20	-11	-16	-6.9	-3.9	-5.4	-0.6	0.4	-0.1	-2	0.7	-0.8
Pirimicarb	-5	-1.1	-2.8	-3.8	-2.3	-3.1	-4.9	-3.4	-4.3	-5.1	-0.3	-2.7

Acetamiprid	-23	-5.3	-13	-12	-2.3	-8.3	-19	-16	-17	10	16	14
Clothianidin	-24	9.2	-5.4	-4.2	7.7	0.7	-11	0.3	-4.3	-6.0	-2.2	-3.7
Dinotefuran*	-	-	-	-9.8	19	8.5	2.9	17	7.8	-1.8	0.2	-0.5
Imidacloprid	-19	-0.1	-7.3	-3.4	5.4	0.9	3.3	17	8.7	-0.8	9.5	3.9
Thiacloprid	12	23	15	-12	9.5	3.1	0.1	2.7	1.4	1.3	10	5.2
Thiamethoxam	-26	-5	-16	-9.1	1.0	-3.6	-3.8	1.8	-1.8	-2.7	0.4	-0.7
Diazinon	-7.5	0.2	-2.6	-4.2	7.3	1.8	-1.9	7.3	2.1	7	16	11
Profenofos*	-	-	-	-	-	-	-31	7.7	-6.6	-15	38	3.1
Dichlorvos*	-	-	-	-14	23	7.4	-5.5	16	4.9	4.3	14	9.6
Dimethoate	-0.3	8.2	3.3	-3.9	3.7	0.5	0.4	12	5.1	-8.1	-0.5	-5.5
Isofenphos-methyl	-3.3	26	9.6	0.9	19	12	-18	9.6	-5.5	-3.6	12	5.4
Malathion	-5.8	25	10	-5.9	3.2	-1.5	-16	27	9.7	4.4	17	8.9
Omethoate	-4.6	21	11	-2.3	4.0	-0.1	-2.8	3.4	1.2	-1.1	0.3	-0.3
Tolfenpyrad	-25	-0.5	-15	-9.8	11	-0.5	-14	1.8	-3.5	-7.8	0.5	-3.8
Chlorobenzuron*	-	-	-	-	-	-	-27	-0.3	-18	-6.5	12	2.6
Etoxazole	1.3	8	4.5	3.1	12	8.5	-1.4	9.4	1.2	7.1	27	18
Pyriproxyfen	-1.8	15	6.8	-6.5	-0.9	-2.6	1.1	4.6	3	0.6	3.8	2.4
Tebufenozide	5.0	21	12	-10	1.3	-2.2	-5.4	3.3	-1.2	-14	3.3	-9
Cyproconazole	-12	20	8.6	-10.1	3.2	-4	0.6	12	6.6	-4.8	-1.9	-3.6
Difenoconazole	-15	14	0.8	-5.7	9.8	-0.3	-4.9	0.1	-2.9	-8.5	0.6	-2.6
Diniconazole	-18	6.2	-6.5	3.3	9.8	6.6	-1.0	4.8	1.3	-7.1	-2.9	-4.9
Epoxiconazole	2.6	23	9.9	-10	4.7	-2	-9.0	8.9	-3.4	-9.3	0.5	-3
Flusilazole	-16	5	-3.3	-8.2	2.9	-2.6	4.5	12	8.2	-9.9	9.0	-0.4
Myclobutanil	-7.8	10	3	-19	-6.4	-13	-15	14	0.5	-4.3	5.0	1.4
Propiconazol	-16	20	-0.3	-13	1.5	-4.8	-0.5	13	5.7	-0.8	9.6	3.2
Tebuconazole	-18.1	23	1.3	-15	18	7.7	-16	-3.1	-11	-12	0	-6.9
Triadimefon	1.2	11	6.6	1	11	6.2	-4.5	4.3	0.5	-4.7	0.2	-2.4
Triadimenol	-3.4	17	4.1	-15	6.1	-3	-4.0	4.2	0.5	-6.1	0	-3
Triazophos	9.3	27	21	-4.4	9.9	2.3	-0.1	4.1	1.7	0	11	6.8
Tricyclazole	-0.9	1.5	0.3	-0.7	5.7	1.8	-1.3	2.4	1.1	-0.2	1.2	0.6
Azoxystrobin	-7.6	8.5	-0.4	-5.6	-1.2	-3.2	-10	5.3	-2.5	-16	-8.2	-11
Fluoxastrobin	-13	24	3.1	0.8	9.1	3.3	-7.1	2.3	-2.3	-5.9	-0.2	-2.6
Kresoxim-methyl	-8.4	12	4.0	3.3	16	7.3	0.9	28	13	-2.1	17	6.3

Picoxystrobin	-3.1	5.1	-0.7	-2.7	7.4	0.1	0.6	8.5	4.1	0.1	3.1	0.9
Pyraclostrobine	-2.6	6	2.1	6.4	14	8.8	-0.4	2.5	1.0	0.7	11	7.1
Trifloxystrobin	-0.8	15	6.5	-6	-1	-3.1	-4.1	13	1.7	7.9	16	12
Prochloraz	-8.3	7.6	-1.6	-4	24	15	-2.5	29	9.6	-15	3.2	-9
Triflumizole	-7.1	8.7	-0.7	-0.8	9.3	3	-3.8	5.9	2.4	-4.4	2.0	-0.4
Imazalil	-10	17	6.6	-1.5	4.4	1.8	-0.2	2.9	1.2	-2.5	0.2	-0.9
Cyprodinil	-12	5.1	-4.0	0	5.0	2.7	-4.3	6.9	2.3	-8	5.4	-0.4
Pyrimethanil	-17	-1.2	-10	-0.6	15	8.8	-2	10	2.4	-6.6	2	-0.5
Carbendazim	-16	-0.5	-4.9	-4.3	-1.4	-3.2	-1.7	-0.6	-1.1	-1.0	1.0	0.1
Thiophanate-methyl	-20	7.9	-8.2	-23	22	-2.3	-21	17	2.4	1.6	14	5.9
Boscalid	-14	26	2.5	-23	-7.2	-16	-8.9	27	9.1	-5.3	6.1	-0.3
Dimethomorph	-4.2	26	6.7	-26	-13	-21	-16	-4.4	-9.5	-6.2	19	1.6
Metalaxyl	-15	-4.1	-10	-1.7	8.3	3.9	-9.0	0.5	-3.8	-16	-11	-14
Oxathiapiprolin	-11	16	2.9	-17	5.4	-6.2	-8.4	1.0	-2.6	-9.9	-1.1	-6.1
Isoprothiolane	-11	18	1.6	-5.5	3.0	-0.1	-2.5	0.2	-1.1	5.5	24	17

* means that the pesticide with defect in the calculation of relative deviation of ion ratio at low or low-medium concentration due to the insufficient response of qualitative ion.

Table S12 Relative deviation of ion ratio of pesticides in WWE samples (%)

Chemical name	DW1	DW2	DW3	DW4	DW5	DW6	DW7	DW8	DW9	IW1	IW2	IW3
Penoxsulam	-0.6	-11	-	-	-	6.4	-	-17	0	-	-3.1	-10
Acetochlor	20	-	-	-	-	-	-	-	-	-	-	-
Nicosulfuron	-21	9.7	-11	19	-	-	-	9.8	-2.2	-	1.5	-2.4
Ametryn	-2.3	-2.7	8.6	1.8	-	19	3.6	-1.4	5.0	-	1.8	-9.5
Atrazine	-	-	-	-	-	-	-	-	-	-	-	-
Propiconazole	11	4.4	21	-19	2	-2	11	-12	10	-	7.9	15
Tebuconazole	1.2	8.1	9.3	1.2	1	-0.7	8.8	-17	-13	-	-	2.6
Terbutryn	-	-	-	-	-	-	-	-	-	-	-2.4	-
Thiacloprid	-	-	-	-	-	-	-	-	-	-	-20	-
Bensulfuron-methyl	-	-	-1.6	-	-	-	-	-16	-	-	2.8	-
Florasulam	-	-	-	-	-	-	-	-	-	-	6.1	-
Paclobutrazol	8.0	4.8	12	14	16	10	2.1	9.0	9.0	1.1	10	-1.6
Pyrimethanil	-22	2.0	-3.0	8.7	15.4	0.4	-2.0	1.3	-13	-	-	8.4
Ethametsulfuron-methyl	-	-	-	-	-	-	-	-	-	-	-29	-
MCPA	-	-	-	-	-	-	-	-	-	29	2.4	-
Mesotrione	-	-	-	-	-	-	-	-	-	-	-9.9	-
Fomesafen	-17	-25	-	-	-8.7	-33	-	-	-31	-	-	-36
Fluroxypyr	-	-	4.0	-	-	-	-	-	-	-	-7.3	-
Prochloraz	-16	-	14.1	18.5	-	-	-7.6	-3.7	-11	-	-24	-
Metalaxyl	0.2	7.9	6.6	7.1	1.3	1.2	1.3	1	-6.5	-	9.0	6.3
Imidacloprid	-8.8	18	18	25	6.2	21	7.1	20	15	-	10	10
2,4-D												
Mefenacet	-12	-	-3.4	-	-	-	-	0.8	16	-	-0.3	-
Bentazone	-4.6	3.9	-0.3	1.8	6.2	-17	-1.1	3.7	3.7	-	-	2.7
Pyrazosulfuron-ethy	-	-	-	-	-	-	-	-	-	-	19	-15
Carbofuran	-6.0	-2.9	0.6	-7.9	8.6	0.4	0.3	4.4	7.4	-	-3.2	-0.1
Isoprothiolane	0.4	3.8	5.6	4.8	7.6	7.6	-2.4	0	-2.9	-	-1.8	1.6
Acetamiprid	6.2	-10	-4.0	-6.2	-6.1	-5.1	-0.2	1.3	11	-4.0	-9.1	6.9
Isoprocab	-	-	-19	-6.2	10	-6.4	-8.8	13	-7.7	-	-	-
Thiophanate-methyl	-	-	-	-7.8	-	-	-	-	13	-	13	26
Diazinon	-11	-4.2	-	-	-	4	-	-	-1	-	-	-

Table S13 Linearity coefficient of each pesticide in the two ranges

Chemical name	R ²	Range (ng/L)	R ²	Range (ng/L)
Pacllobutrazol	0.9990	0.1–100	0.9998	100–2500
Acetochlor	0.9995	0.1–100	0.9943	100–2500
Alachlor	0.9964	0.1–100	0.9955	100–2500
Butachlor	0.9918	0.1–100	0.9996	100–2500
Metolachlor	0.9975	0.1–100	0.9946	100–2500
Pretilachlor	0.9962	0.1–100	0.9999	100–2500
Ametryn	0.9998	0.1–100	0.9996	100–2500
Atrazine	0.9998	0.1–100	0.9934	100–2500
Atrazine-desethyl	1.0000	0.1–100	0.9962	100–2500
Atrazine-desisopropyl	0.9997	0.1–100	0.9915	100–2500
Cyanazine	0.9998	0.1–100	0.9989	100–2500
Prometryn	0.9998	0.1–100	0.9952	100–2500
Simazine	0.9998	0.1–100	0.9994	100–2500
Terbuthylazine	0.9996	0.1–100	0.9939	100–2500
Terbutryn	0.9997	0.1–100	0.9970	100–2500
Bensulfuron-methyl	0.9974	0.1–100	0.9991	100–2500
Ethametsulfuron-methyl	0.9980	0.1–100	0.9965	100–2500
Nicosulfuron	0.9992	0.1–100	0.9995	100–2500
Pyrazosulfuron-ethy	0.9987	0.1–100	0.9993	100–2500
Tribenuron-methyl	0.9985	0.1–100	0.9937	100–2500
Diflufenican	0.9879	0.1–100	0.9932	100–2500
Diuron	0.9999	0.1–100	0.9959	100–2500
Isoproturon	0.9994	0.1–100	0.9927	100–2500
Chlortoluron	0.9993	0.1–100	0.9977	100–2500
Flufenacet	0.9991	0.1–100	0.9875	100–2500
Isoxaflutole	0.9990	0.1–100	0.9839	100–2500
Mefenacet	0.9984	0.1–100	0.9958	100–2500
Clodinafop-propargyl	0.9939	0.1–100	0.9978	100–2500
Haloxypop-r-methyl	0.9978	0.1–100	0.9947	100–2500
Quizalofop-p-ethyl	0.9959	0.1–100	0.9935	100–2500
Imazaquin	0.9999	0.1–100	0.9996	100–2500
Imazethapyr	0.9996	0.1–100	0.9940	100–2500
Butralin	0.9893	0.1–100	0.9937	100–2500
Carfentrazone-ethyl	0.9964	0.1–100	0.9979	100–2500
Pinoxaden	0.9903	0.1–100	0.9977	100–2500
Fluazinam	0.9929	0.1–100	0.9981	100–2500
Fluroxypyr	0.9998	0.1–100	0.9962	100–2500
Metribuzin	0.9993	0.1–100	0.9985	100–2500
Amicarbazone	0.9999	0.1–100	0.9987	100–2500
Florasulam	0.9994	0.1–100	0.9972	100–2500
Penoxsulam	0.9996	0.1–100	0.9980	100–2500
Mesotrione	0.9995	0.1–100	0.9911	100–2500
Fomesafen	0.9994	0.1–100	0.9994	100–2500
Napropamide	0.9987	0.1–100	0.9993	100–2500
Propyzamide	0.9901	0.1–100	0.9951	100–2500
2,4-D	0.9971	0.1–100	0.9994	100–2500
MCPA	0.9997	0.1–100	0.9979	100–2500

Bentazone	0.9971	0.1–100	0.9960	100–2500
Propham	0.9998	0.1–100	0.9998	100–2500
Pendimethalin	0.9915	0.1–100	0.9997	100–2500
Diazinon	0.9970	0.1–100	0.9990	100–2500
Propoxur	0.9986	0.1–100	0.9999	100–2500
Carbofuran	0.9994	0.1–100	0.9998	100–2500
3-hydroxy-carbofuran	0.9995	0.1–100	0.9999	100–2500
Aldicarb	0.9983	0.1–100	0.9880	100–2500
Aldicarb-sulfone	0.9949	0.1–100	0.9999	100–2500
Aldicarb-sulfoxide	0.9916	0.1–100	0.9985	100–2500
Carbaryl	0.9997	0.1–100	0.9997	100–2500
Diethofencarb	0.9995	0.1–100	0.9989	100–2500
Fenobucarb	0.9997	0.1–100	0.9979	100–2500
Indoxacarb	0.9924	0.1–100	0.9963	100–2500
Isoprocarb	0.9958	0.1–100	0.9995	100–2500
Methomyl	0.9946	0.1–100	0.9999	100–2500
Pirimicarb	0.9971	0.1–100	0.9976	100–2500
Acetamiprid	0.9992	0.1–100	0.9998	100–2500
Clothianidin	0.9967	0.1–100	0.9998	100–2500
Dinotefuran	0.9946	0.1–100	0.9971	100–2500
Imidacloprid	0.9994	0.1–100	0.9955	100–2500
Thiacloprid	0.9947	0.1–100	0.9992	100–2500
Thiamethoxam	0.9995	0.1–100	0.9999	100–2500
Profenofos	0.9949	0.1–100	0.9984	100–2500
Dimethoate	0.9995	0.1–100	0.9995	100–2500
Isofenphos-methyl	0.9937	0.1–100	0.9745	100–2500
Malathion	0.9963	0.1–100	0.9849	100–2500
Omethoate	0.9997	0.1–100	0.9921	100–2500
Tolfenpyrad	0.9871	0.1–100	0.9976	100–2500
Chlorobenzuron	0.9977	0.1–100	0.9904	100–2500
Etoxazole	0.9939	0.1–100	0.9975	100–2500
Pyriproxyfen	0.9962	0.1–100	0.9961	100–2500
Tebufozide	0.9968	0.1–100	0.9965	100–2500
Cyproconazole	0.9958	0.1–100	0.9982	100–2500
Difenoconazole	0.9971	0.1–100	0.9996	100–2500
Diniconazole	0.9988	0.1–100	0.9908	100–2500
Epoxiconazole	0.9998	0.1–100	0.9995	100–2500
Flusilazole	0.9996	0.1–100	0.9980	100–2500
Myclobutanil	0.9929	0.1–100	0.9995	100–2500
Propiconazol	0.9983	0.1–100	0.9978	100–2500
Tebuconazole	0.9958	0.1–100	0.9981	100–2500
Triadimefon	0.9995	0.1–100	0.9974	100–2500
Triadimenol	0.9985	0.1–100	0.9957	100–2500
Triazophos	0.9968	0.1–100	0.9989	100–2500
Tricyclazole	0.9951	0.1–100	0.9876	100–2500
Azoxystrobin	0.9959	0.1–100	0.9944	100–2500
Fluoxastrobin	0.9996	0.1–100	0.9987	100–2500
Kresoxim-methyl	0.9914	0.1–100	0.9883	100–2500
Picoxystrobin	0.9984	0.1–100	0.9908	100–2500

Pyraclostrobin	0.9981	0.1–100	0.9989	100–2500
Trifloxystrobin	0.9972	0.1–100	0.9965	100–2500
Prochloraz	0.9990	0.1–100	0.9984	100–2500
Triflumizole	0.9912	0.1–100	0.9983	100–2500
Imazalil	0.9933	0.1–100	0.9984	100–2500
Cyprodinil	0.9977	0.1–100	0.9980	100–2500
Pyrimethanil	0.9944	0.1–100	0.9994	100–2500
Carbendazim	0.9999	0.1–100	0.9997	100–2500
Thiophanate-methyl	0.9946	0.1–100	0.9968	100–2500
Boscalid	0.9939	0.1–100	0.9942	100–2500
Dimethomorph	0.9988	0.1–100	0.9988	100–2500
Metalaxyl	0.9970	0.1–100	0.9930	100–2500
Oxathiapiprolin	0.9938	0.1–100	0.9988	100–2500
Isoprothiolane	0.9974	0.1–100	0.9908	100–2500

Table S14 MDLs and MQLs of each pesticide in the three matrixes

Chemical name	MDL (ng/L)			MQL (ng/L)		
	DW	SW	WWE	DW	SW	WWE
Paclobutrazol	0.03	0.4	0.6	0.1	1.3	1.9
Acetochlor	0.7	2.1	3.2	2.3	6.9	11
Alachlor	1.0	1.0	1.3	3.2	3.4	4.4
Butachlor	0.1	0.6	0.8	0.3	1.9	2.6
Metolachlor	0.2	0.3	0.3	0.7	1.0	1.0
Pretilachlor	0.08	0.2	0.2	0.3	0.6	0.7
Ametryn	0.05	0.1	0.2	0.2	0.3	0.8
Atrazine	0.08	0.2	1.8	0.3	0.8	5.8
Atrazine-desethyl	0.3	2.0	2.2	0.9	6.6	7.4
Atrazine-desisopropyl	0.07	0.4	0.7	0.2	1.4	2.2
Cyanazine	0.02	0.1	0.1	0.07	0.4	0.4
Prometryn	0.07	0.1	0.2	0.2	0.3	0.5
Simazine	0.07	0.3	0.4	0.2	1.0	1.5
Terbutylazine	0.06	0.2	0.2	0.2	0.5	0.7
Terbutryn	0.05	0.6	1.5	0.2	2.1	5.0
Bensulfuron-methyl	0.2	0.4	0.5	0.7	1.4	1.7
Ethametsulfuron-methyl	0.02	0.08	0.1	0.07	0.3	0.4
Nicosulfuron	0.1	0.1	0.1	0.4	0.3	0.3
Pyrazosulfuron-ethyl	0.05	0.1	0.2	0.2	0.5	0.7
Tribenuron-methyl	0.6	0.1	0.2	1.9	0.4	0.6
Diflufenican	0.05	0.4	0.7	0.2	1.2	2.3
Diuron	0.1	0.2	0.7	0.4	0.8	2.5
Isoproturon	0.3	3.6	6.2	1.0	12	20
Chlortoluron	0.07	0.2	0.3	0.2	0.6	1.0
Flufenacet	0.06	0.1	0.1	0.2	0.4	0.4
Isoxaflutole	0.4	0.7	1.2	1.5	2.4	4.0
Mefenacet	0.09	0.10	0.1	0.3	0.4	0.5
Clodinafop-propargyl	0.01	0.7	1.0	0.03	2.4	3.3
Haloxypop-r-methyl	0.2	1.0	1.2	0.6	3.3	4.0
Quizalofop-p-ethyl	0.08	0.2	0.8	0.3	0.8	2.6
Imazaquin	0.05	0.2	0.4	0.2	0.8	1.5
Imazethapyr	0.03	0.2	0.2	0.1	0.5	0.7
Butralin	0.7	1.1	1.4	2.4	3.5	4.5
Carfentrazone-ethyl	0.05	0.3	0.4	0.2	1.0	1.3
Pinoxaden	0.02	0.1	0.1	0.07	0.3	0.4
Fluazinam	0.1	0.3	0.4	0.5	0.9	1.2
Fluroxypyr	0.2	3.1	6.4	0.7	10	21
Metribuzin	0.1	1.9	2.8	0.5	6.1	9.2
Amicarbazone	0.03	0.7	0.4	0.08	2.3	1.3
Florasulam	0.2	0.8	1.3	0.7	2.7	4.2
Penoxsulam	0.2	0.3	0.4	0.7	1.0	1.3
Mesotrione	0.6	2.0	3.5	2.0	7	12
Fomesafen	0.3	0.5	0.5	1.1	1.5	1.6
Napropamide	0.2	0.3	0.4	0.5	1.1	1.5
Propyzamide	0.3	0.6	0.7	0.8	1.8	2.2
2,4-D	0.6	2.1	2.8	1.9	7.0	9.3

MCPA	0.09	0.9	1.9	0.3	3.0	6.3
Bentazone	0.02	0.1	0.1	0.08	0.3	0.4
Propham	1.4	2.7	3.8	4.6	9	12
Pendimethalin	0.4	1.0	1.4	1.4	3.4	4.5
Diazinon	0.02	0.06	0.08	0.06	0.2	0.3
Propoxur	0.01	0.2	0.3	0.04	0.7	1.0
Carbofuran	0.01	0.2	0.3	0.04	0.6	0.9
3-hydroxy-carbofuran	0.03	1.1	2.3	0.09	3.6	7.5
Aldicarb	0.14	1.2	3.4	0.4	3.8	11
Aldicarb-sulfone	0.08	5.2	5.8	0.3	17	19
Aldicarb-sulfoxide	0.04	0.6	0.9	0.1	1.9	2.9
Carbaryl	0.02	0.8	0.9	0.07	2.5	2.9
Diethofencarb	0.04	0.2	0.3	0.1	0.7	0.9
Fenobucarb	0.09	0.4	0.6	0.3	1.3	2.1
Indoxacarb	1.6	1.6	2.1	5.3	5.2	6.9
Isoprocarb	0.1	0.3	0.4	0.5	1.1	1.5
Methomyl	0.02	0.2	0.2	0.07	0.5	0.7
Pirimicarb	0.02	0.2	0.2	0.07	0.5	0.8
Acetamiprid	0.02	0.3	0.4	0.07	0.9	1.4
Clothianidin	0.02	0.2	0.3	0.06	0.5	1.2
Dinotefuran	0.8	2.1	3.8	2.7	6.9	13
Imidacloprid	0.5	1.8	2.9	1.5	5.9	9.5
Thiacloprid	0.1	0.5	0.8	0.4	1.6	2.7
Thiamethoxam	0.2	0.3	0.5	0.5	0.9	1.7
Profenofos	0.2	0.9	1.3	0.6	3.1	4.4
Dichlorvos	1.0	4.2	4.9	3.3	14	16
Dimethoate	0.1	0.2	0.2	0.4	0.5	0.8
Isofenphos-methyl	1.0	1.1	1.4	3.3	3.8	4.5
Malathion	0.1	0.2	0.4	0.3	0.8	1.3
Omethoate	0.1	0.3	0.5	0.3	1.1	1.8
Tolfenpyrad	0.1	0.3	0.5	0.5	1.1	1.8
Chlorobenzuron	0.4	1.1	1.6	1.4	3.6	5.4
Etoxazole	0.01	0.02	0.02	0.04	0.06	0.08
Pyriproxyfen	0.05	0.3	0.5	0.2	1.1	1.7
Tebufenozide	0.07	0.3	0.4	0.2	0.9	1.2
Cyproconazole	0.02	0.1	0.1	0.06	0.4	0.5
Difenoconazole	0.05	0.1	0.2	0.2	0.4	0.5
Diniconazole	0.2	0.3	0.4	0.5	0.9	1.2
Epoxiconazole	0.2	0.6	1.0	0.6	2.0	3.2
Flusilazole	0.4	0.6	0.6	1.3	2.0	2.1
Myclobutanil	0.06	0.1	0.1	0.2	0.4	0.4
Propiconazol	0.03	0.2	0.3	0.1	0.6	0.9
Tebuconazole	0.1	0.9	1.2	0.4	3.0	4.0
Triadimefon	0.1	0.2	0.2	0.5	0.6	0.8
Triadimenol	0.1	0.2	0.4	0.4	0.7	1.4
Triazophos	0.08	0.2	0.3	0.3	0.6	0.9
Tricyclazole	0.08	1.1	1.6	0.3	3.5	5.3
Azoxystrobin	0.04	0.3	0.5	0.1	1.1	1.8
Fluoxastrobin	0.1	0.2	0.3	0.4	0.7	1.0

Kresoxim-methyl	0.03	0.1	0.3	0.09	0.4	0.8
Picoxystrobin	0.05	0.07	0.09	0.2	0.2	0.3
Pyraclostrobine	0.05	0.1	0.2	0.2	0.4	0.5
Trifloxystrobin	0.07	0.1	0.2	0.2	0.4	0.6
Prochloraz	0.1	0.2	0.4	0.5	0.7	1.4
Triflumizole	0.2	0.2	0.3	0.7	0.7	0.9
Imazalil	0.09	1.0	1.9	0.3	3.4	6.3
Cyprodinil	0.05	0.3	0.4	0.2	1.0	1.3
Pyrimethanil	0.05	0.2	0.4	0.2	0.8	1.3
Carbendazim	0.04	0.08	0.5	0.1	0.3	1.7
Thiophanate-methyl	0.4	1.5	2.2	1.2	5.0	7.4
Boscalid	0.3	0.2	0.2	0.9	0.6	0.6
Dimethomorph	0.04	0.2	0.2	0.1	0.5	0.6
Metalaxyl	0.04	0.2	0.3	0.1	0.7	1.1
Oxathiapiprolin	0.06	0.1	0.1	0.2	0.4	0.4
Isoprothiolane	0.1	0.2	0.2	0.4	0.7	0.8

Table S15 Intra-day and inter-day precision of each pesticide

Chemical name	Intra-day precision (% , n=5)												Inter-day precision (% , n=15)		
	5 ng/L			25 ng/L			100 ng/L			1000 ng/L			25 ng/L		
	DW	SW	WWE	DW	SW	WWE	DW	SW	WWE	DW	SW	WWE	DW	SW	WWE
Paclobutrazol	8.0	4.7	3.2	3.2	4.3	7.8	2.2	6.3	5.0	1.8	9.9	2.5	8.5	13	11
Acetochlor	9.5	16	14	5.2	7.4	10	3.0	6.4	4.3	8.9	9.1	9.2	8.6	11	12
Alachlor	6.7	8.6	12	6.3	4.6	11	5.0	4.0	3.7	8.2	9.6	8.8	11	11	9.4
Butachlor	5.0	9.6	18	3.1	8.4	13	9.7	6.6	15	3.9	5.5	11	8.9	13	9.9
Metolachlor	5.5	11	7.7	6.3	14	11	4.3	8.7	11	2.0	2.8	5.9	4.6	9.9	7.7
Pretilachlor	6.7	6.7	13	2.3	7.3	13	8.3	6.7	17	1.7	6.0	17	3.6	10	8.7
Ametryn	2.9	1.5	5.2	5.1	5.5	1.3	3.1	3.9	2.1	1.2	2.1	1.9	8.9	5.6	4.9
Atrazine	4.7	19	13	2.8	12	4.8	2.7	7.7	3.5	0.4	1.3	1.7	7.4	6.6	5.5
Atrazine-desethyl	2.5	7.3	13	0.5	1.9	1.6	3.4	6.2	4.6	0.8	0.4	3.6	4.0	8.1	9.8
Atrazine-desisopropyl	9.0	13	11	3.8	6.6	4.2	4.2	5.6	4.5	1.5	2.8	2.2	7.8	7.0	16
Cyanazine	7.2	6.4	5.9	5.7	6.8	11	8.9	8.6	10	2.5	4.5	4.9	7.0	11	6.8
Prometryn	3.2	5.6	3.8	3.4	6.0	1.8	3.1	4.4	2.7	1.2	1.7	1.7	11	5.0	5.8
Simazine	3.8	6.3	11	3.1	2.8	3.1	3.2	4.3	1.3	1.4	2.3	3.2	4.9	5.5	4.8
Terbutylazine	1.6	5.5	3.4	3.2	7.1	3.3	3.2	6.7	5.4	3.9	1.7	3.3	7.2	7.5	6.8
Terbutryn	4.9	6.5	4.5	4.5	7.5	4.4	3.7	3.6	2.9	0.9	1.2	4.0	16	15	16
Bensulfuron-methyl	13	15	5.4	9.5	11	12	7.7	8.7	8.5	3.1	3.8	4.4	11	12	12
Ethametsulfuron-methyl	0.8	3.3	2.2	2.5	4.2	4.0	3.0	4.9	5.5	1.9	1.1	7.4	13	8.6	26
Nicosulfuron	2.9	6.7	1.7	4.1	2.9	2.1	1.7	1.9	1.5	1.6	1.2	5.5	11	10	19
Pyrazosulfuron-ethy	4.4	7.2	2.5	5.9	9.6	12	6.4	4.6	8.4	1.7	1.0	4.3	8.0	12	7.5
Tribenuron-methyl	6.3	12	5.3	5.8	6.9	9.4	3.1	2.9	5.6	2.8	3.6	7.6	12	7.6	8.8
Diflufenican	8.8	12	14	3.2	8.9	8.5	6.0	3.3	12	3.7	5.2	2.5	10	8.8	7.5
Diuron	5.6	12	5.9	1.8	3.4	7.1	9.1	5.1	2.4	2.4	2.5	3.9	7.0	2.9	5.5
Isoproturon	5.5	11	3.0	5.5	4.7	5.7	6.6	7.3	6.8	0.9	4.6	4.5	8.8	7.2	11
Chlortoluron	6.4	3.2	5.9	3.8	8.3	11	12	9.7	11	7.4	8.3	5.0	7.7	9.9	5.8
Flufenacet	5.0	4.3	15	9.9	4.5	15	4.8	7.4	6.7	0.9	3.9	3.7	4.0	10	12
Isoxaflutole	18	19	17	11	6.0	9.5	4.8	3.8	2.5	3.7	3.5	7.2	18	13	20
Mefenacet	5.7	2.5	3.9	4.0	6.6	8.9	3.1	8.4	9.1	1.7	3.9	6.8	9.7	11	7.0
Clodinafop-propargyl	5.3	8.9	12	2.2	2.3	8.0	7.5	11	18	11	16	12	12	9.6	12
Haloxypop-r-methyl	6.5	18	11	8.9	13	10	7.6	7.1	12	4.1	5.4	8.0	5.7	12	13

Quizalofop-p-ethyl	7.4	5.3	12	3.4	5.8	12	8.3	10.0	10	3.7	2.3	10.0	8.4	13	21
Imazaquin	6.7	5.2	5.5	3.8	5.8	2.0	4.0	4.2	4.1	1.8	1.7	3.6	13	9.1	14
Imazethapyr	8.1	1.7	5.3	4.5	6.1	1.1	4.3	6.4	11	2.7	2.2	1.4	11	27	14
Butralin	17	13	20	13	11	22	8.6	5.1	20	8.8	4.4	20	14	11	7.5
Carfentrazone-ethyl	10	19	18	6.7	8.3	15	14	13	12	15	12	14	10	9.7	15
Pinoxaden	2.9	9.4	5.2	2.1	4.6	3.4	2.2	9.9	15	8.0	4.1	17	17	11	9.5
Fluazinam	6.4	4.7	15.4	8.5	6.7	19.0	9.9	7.6	18	8.5	6.4	15	13	12	12
Fluroxypyr	22	-	-	7.5	6.3	6.8	4.7	18	18	11	8.4	12	12	18	19
Metribuzin	2.5	12	5.2	1.9	4.3	4.7	2.4	3.4	8.5	2.4	2.5	1.1	9.9	16	11
Amicarbazone	7.8	1.6	6.4	3.9	6.6	3.5	2.3	3.4	4.7	1.3	2.8	7.5	7.2	9.4	16
Florasulam	9.6	9.8	6.3	5.4	4.6	6.3	8.5	4.1	4.6	1.0	3.3	3.6	7.0	9.1	12
Penoxsulam	8.6	4.7	2.9	4.2	14	3.5	2.8	6.5	6.5	3.4	0.5	12	15	7.5	11
Mesotrione	13	8.6	4.4	5.4	17	11	7.0	7.5	19	5.7	3.7	3.3	6.4	26	13
Fomesafen	1.2	17	12	2.0	9.6	9.0	6.2	7.4	14	7.5	5.6	5.3	18	14	14
Napropamide	5.8	8.3	5.7	5.0	8.9	10.0	6.1	6.9	11	1.2	3.0	5.7	5.3	11	6.9
Propyzamide	5.6	3.1	19	7.6	7.1	9.4	3.7	10	5.2	3.3	3.3	3.5	9.6	9.1	13
2,4-D	5.5	12	17	7.2	12	20	9.9	8.9	8.6	11	7.8	11	15	16	9.0
MCPA	12	13	15	6.8	13	6.7	11	6.7	11	9.2	5.2	11	16	17	11
Bentazone	6.9	19	4.3	2.5	6.9	5.5	7.4	3.6	8.2	3.6	3.7	4.2	15	21	12
Propham	10	5.0	9.0	4.8	3.3	6.9	2.1	5.0	6.3	3.2	3.6	5.5	10	6.9	9.8
Pendimethalin	8.1	10.0	18	7.2	10	19	4.3	7.0	17	4.3	3.5	8.9	19	9.0	3.6
Propoxur	6.1	3.9	6.3	2.8	2.0	2.3	2.2	2.8	6.1	2.4	1.5	6.8	22	12	9.5
Carbofuran	4.7	3.8	3.2	2.7	4.5	1.3	2.8	3.5	3.7	0.5	2.3	4.9	8.9	8.2	8.9
3-hydroxy-carbofuran	7.3	9.8	9.0	7.3	15	12	4.4	3.3	10	4.2	7.8	9.1	8.0	9.9	17
Aldicarb	15	12	13	15	13	8.2	9.0	5.2	10	11	7.8	16	23	27	23
Aldicarb-sulfone	8.8	2.0	1.9	4.9	1.6	3.9	6.7	7.5	9.8	4.4	3.5	5.5	15	16	18
Aldicarb-sulfoxide	8.3	3.0	13	8.8	5.9	14	8.4	7.9	21	6.1	10	8.5	26	20	28
Carbaryl	6.3	8.8	13	8.2	6.0	10	4.4	6.6	5.8	3.2	8.4	5.3	9.5	8.3	9.4
Diethofencarb	14	12	6.8	7.6	5.3	9.9	4.9	6.8	6.0	3.0	5.9	1.8	10	12	10
Fenobucarb	12	10	20	6.6	7.2	11	5.6	12	5.7	6.3	9.3	4.5	16	8.6	8.5
Indoxacarb	8.8	8.8	13	7.0	9.5	8.6	0.9	9.3	10	3.9	7.2	7.6	14	11	12
Isoprocarb	10	14	16	2.4	2.4	15	14	6.1	8.3	4.2	3.3	7.6	13	9.8	10
Methomyl	3.9	1.4	18	1.1	2.9	13	3.5	4.7	13	1.5	3.6	3.5	17	13	28

Pirimicarb	2.5	3.4	5.4	2.9	6.4	6.9	3.1	3.6	3.3	1.4	1.1	4.4	11	9.8	18
Acetamiprid	1.8	1.0	5.1	1.1	1.5	2.2	1.7	2.6	1.8	0.7	0.6	0.8	7.3	7.0	7.3
Clothianidin	9.2	4.7	6.8	5.4	14	14	5.9	4.8	7.1	4.7	5.0	9.3	14	9.9	14
Dinotefuran	10	4.0	11	7.6	2.2	9.0	7.8	14	11	5.8	6.7	11	14	12	13
Imidacloprid	3.9	7.4	7.4	1.7	5.4	14	4.7	5.2	5.0	1.8	3.5	9.6	12	9.1	18
Thiacloprid	4.5	3.8	3.0	2.6	2.1	3.5	2.5	1.3	2.6	2.5	2.0	4.8	14	9.1	9.5
Thiamethoxam	7.5	4.1	4.6	4.0	2.8	3.9	0.7	2.1	5.6	5.4	1.6	1.1	9.3	20	13
Diazinon	2.4	2.2	1.2	3.4	7.0	3.8	4.1	3.4	3.6	2.7	2.1	0.8	12	7.7	7.9
Profenofos	10	17	18	10	5.8	5.7	3.6	9.3	2.7	5.5	2.1	2.7	16	12	21
Dichlorvos	6.3	6.9	5.3	6.1	10	5.5	4.6	5.0	5.0	3.8	3.6	3.6	13	11	9.3
Dimethoate	2.5	4.7	5.8	3.4	1.2	6.7	1.8	0.6	6.7	5.4	12	9.9	6.6	3.8	12
Isofenphos-methyl	7.3	11	18	7.7	7.7	12	4.2	4.6	11	4.7	3.5	9.3	9.4	6.5	6.9
Malathion	12	6.8	14	6.0	6.1	7.1	11	3.1	3.2	3.1	4.0	6.9	13	6.8	6.7
Omethoate	4.3	2.2	6.6	1.9	0.5	3.5	0.8	2.1	2.2	1.0	1.2	0.8	7.4	5.3	7.4
Tolfenpyrad	14	-	-	7.0	7.1	14	7.4	1.7	16	10.0	7.7	6.5	16	20	14
Chlorobenzuron	20	18	20	4.3	21	13	7.2	11	1.8	3.4	2.7	2.9	18	16	13
Etoxazole	14	5.9	11	6.1	8.5	5.5	7.1	3.7	13	6.9	4.9	6.5	15	14	14
Pyriproxyfen	8.4	5.2	17	5.5	6.1	5.8	4.1	4.2	14	3.8	5.6	12	13	10	9.8
Tebufozide	6.5	8.2	9.8	4.7	8.0	11	4.3	9.6	5.7	4.9	5.4	4.5	4.0	12	8.7
Cyproconazole	4.5	8.5	12	6.0	3.4	9.7	5.3	2.6	6.6	3.7	5.8	5.5	9.0	9.2	11
Difenoconazole	8.9	6.8	7.7	4.6	9.5	6.2	8.0	7.5	12	3.4	6.5	6.5	7.2	12	12
Diniconazole	3.7	5.1	4.8	5.4	5.9	3.0	4.8	5.4	2.3	3.3	5.4	6.6	7.7	11	13
Epoxiconazole	3.7	2.5	2.9	6.9	5.9	3.9	4.7	4.2	6.7	3.1	4.3	4.1	11	6.6	6.3
Flusilazole	4.2	2.5	11	5.7	1.2	3.4	3.2	4.4	4.0	2.4	7.7	7.0	6.4	11	12
Myclobutanil	6.4	9.0	5.5	3.1	5.7	6.2	8.4	4.2	8.3	2.0	0.7	1.1	18	7.0	8.8
Propiconazol	8.8	12	13	3.4	11	2.9	2.3	4.6	5.3	5.1	5.3	9.0	8.7	12	15
Tebuconazole	6.8	2.7	3.3	3.7	3.9	9.0	2.7	6.2	4.4	2.8	5.5	7.6	8.7	8.3	8.0
Triadimefon	4.6	3.3	3.8	3.6	3.5	5.6	5.3	4.1	3.5	4.3	7.2	4.9	3.2	6.0	9.2
Triadimenol	5.6	7.9	8.6	2.8	2.8	8.3	2.4	3.7	5.9	4.0	6.0	7.1	9.6	16	11
Triazophos	5.4	6.2	5.3	2.3	7.8	13	4.8	10	11	1.8	2.6	3.6	6.6	10	8.7
Tricyclazole	4.3	19	6.8	2.9	9.1	10	5.0	6.7	5.4	6.7	4.5	4.4	8.7	12	12
Azoxystrobin	11	2.7	6.3	2.6	3.0	4.8	3.3	8.8	4.1	3.3	6.9	3.3	8.0	8.6	14
Fluoxastrobin	7.1	4.3	5.1	5.2	8.4	9.6	6.4	9.6	7.6	7.8	11	9.2	5.3	8.5	8.8

Kresoxim-methyl	9.4	5.7	2.4	6.3	5.6	5.7	19	4.2	3.5	3.1	5.7	4.3	8.4	8.9	4.3
Picoxystrobin	10	3.6	7.0	3.6	8.2	13	6.3	6.9	9.6	3.9	6.0	7.9	6.5	11	8.9
Pyraclostrobin	9.7	5.7	11	4.7	7.6	11	7.8	7.3	11	2.8	3.5	9.7	7.3	11	11
Trifloxystrobin	4.4	2.1	9.1	3.5	3.8	8.6	3.4	3.4	6.8	1.8	4.7	7.8	13	8.5	8.0
Prochloraz	4.5	5.5	6.6	5.2	3.8	3.8	4.6	10	10	3.0	5.1	6.1	12	8.5	11
Triflumizole	6.2	7.0	5.1	4.0	4.1	5.2	3.8	3.9	6.2	4.0	5.8	6.0	9.4	5.9	10
Imazalil	4.2	4.4	5.1	2.1	7.8	2.5	3.6	2.3	3.7	1.9	1.5	3.1	8.3	6.8	8.7
Cyprodinil	12	13	8.2	5.1	4.7	9.6	7.1	2.8	6.7	4.0	4.9	2.8	9.4	9.3	10
Pyrimethanil	12	8.9	5.2	5.8	5.5	11	2.1	5.2	6.5	4.5	3.3	1.2	10	12	12
Carbendazim	1.0	2.9	4.9	0.4	3.5	1.6	0.8	2.7	0.7	0.5	0.6	0.2	5.6	3.2	3.1
Thiophanate-methyl	4.9	10	17	7.3	8.8	15	4.2	11	9.2	4.0	5.3	8.1	20	22	21
Boscalid	6.9	4.1	7.5	2.5	8.7	7.9	4.0	9.2	8.1	5.9	9.4	5.8	24	16	15
Dimethomorph	7.1	4.8	14	5.8	5.3	13	8.3	2.9	11	8.0	7.9	11	11	13	11
Metalaxyl	11	6.8	5.1	3.0	2.4	13	5.6	4.9	5.6	4.9	5.4	7.8	9.2	8.7	14
Oxathiapiprolin	5.8	5.9	5.7	5.2	5.2	15	5.2	7.0	8.9	5.8	2.9	6.0	15	11	12
Isoprothiolane	2.7	4.8	5.7	11	9.3	15	3.9	8.1	8.0	1.4	1.7	3.5	5.5	9.9	6.5

Table S16 Concentration (ng/L) and detection frequency (DF, %) of pesticides in WWE samples of 12 WWTPs

Chemical name	WWE of domestic WWTP													WWE of industrial WWTP						
	DW1	DW2	DW3	DW4	DW5	DW6	DW7	DW8	DW9	Min.	Med.	Max.	DF	IW1	IW2	IW3	Min.	Med.	Max.	DF
Pacllobutrazol	5.9	4.6	7.3	8.0	9.1	7.1	11	5.8	4.6	4.6	7.1	11	100	0.6	3.9	3.4	0.6	3.4	3.9	100
Acetochlor	25	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	25	11	BDL	BDL	BDL	BDL	BDL	BDL	0
Metolachlor	7.6	10	86	29	20	14	11	4.4	13	4.4	13	86	100	BDL	11	6.6	BDL	6.6	11	67
Ametryn	38	3.0	0.6	2.4	BDL	0.5	1.6	0.7	1.2	BDL	1.2	38	89	BDL	8.5	0.6	BDL	0.6	8.5	67
Atrazine	172	9.7	1.8	16	6.1	8.5	6.2	12.2	48	1.8	9.7	172	100	35	27	38	27	35	38	100
Prometryn	5.7	3.2	14	3.4	BDL	1.5	4.1	2.3	2.1	BDL	3.2	14	89	BDL	2.6	2.1	BDL	2.1	2.6	67
Simazine	BDL	0.4	BDL	BDL	BDL	BDL	BDL	BDL	0.4	BDL	BDL	0.4	22	BDL	BDL	BDL	BDL	BDL	BDL	0
Terbuthylazine	1.0	143	1.5	0.7	0.8	1.1	0.7	1.2	2.0	0.7	1.1	143	100	BDL	0.2	0.2	BDL	0.2	0.2	67
Terbutryn	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0	BDL	6.9	BDL	BDL	BDL	6.9	33
Bensulfuron-methyl	BDL	BDL	1.6	BDL	BDL	BDL	BDL	0.5	BDL	BDL	BDL	1.6	22	BDL	3.0	BDL	BDL	BDL	3	33
Ethametsulfuron-methyl	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0	BDL	9.6	BDL	BDL	BDL	9.6	33
Nicosulfuron	0.6	0.8	1.6	0.6	BDL	BDL	BDL	1.4	0.8	BDL	0.7	1.6	67	BDL	3.3	0.1	BDL	0.1	3.3	67
Pyrazosulfuron-ethy	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0	BDL	1.9	0.2	BDL	0.2	1.9	67
Diuron	28	41	4.6	3.6	16	8.7	3.6	13	21	3.6	13	41	100	3.9	1,622	8.9	3.9	8.9	1,622	100
Isoproturon	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0	BDL	1,000	BDL	BDL	BDL	1,000	33
Mefenacet	0.1	BDL	0.1	BDL	BDL	BDL	BDL	0.7	0.15	BDL	BDL	0.7	44	BDL	17	BDL	BDL	BDL	17	33
Fluroxypyr	BDL	BDL	43	72	BDL	BDL	BDL	BDL	BDL	BDL	BDL	72	22	BDL	23	BDL	BDL	BDL	23	33
Florasulam	1.7	2.0	1.3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2.0	33	BDL	96	BDL	BDL	BDL	96	33
Penoxsulam	2.2	0.4	BDL	BDL	BDL	0.4	BDL	0.4	0.4	BDL	0.4	2.2	56	BDL	4.4	0.4	BDL	0.4	4.4	67
Mesotrione	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0	BDL	23	BDL	BDL	BDL	23	33
Fomesafen	64	30	BDL	BDL	3861	59	BDL	BDL	32	BDL	30	3861	56	BDL	BDL	16	BDL	BDL	16	33
2,4-D	19	BDL	BDL	BDL	17	2.8	2540.0	BDL	2.8	BDL	2.8	2540	56	24	25	BDL	BDL	24	25	67
MCPA	BDL	BDL	7.6	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	7.6	11.1	16	23	BDL	BDL	16	23	67
Bentazone	25	14	39	9.4	7.0	9.1	10	22	4.4	4.4	10	39	100	BDL	20	6.9	BDL	6.9	20	67
Propoxur	5.1	14	13	13	33	14	9.9	7.8	23	5.1	13	33	100	BDL	2.5	18	BDL	2.5	18	67
Carbofuran	0.3	5.0	24	1.2	0.3	3.3	0.3	1.5	1.4	0.3	1.4	24	100	BDL	4.9	0.3	BDL	0.3	4.9	67
Isoprocab	BDL	BDL	1.8	1.0	0.5	1.3	1.0	0.7	2.0	BDL	1.0	2.0	78	BDL	BDL	BDL	BDL	BDL	BDL	0
Acetamiprid	11	7.7	14	16	18	20	22	23	20	7.7	18	23	100	4.4	30	6.3	4.4	6.3	30	100
Imidacloprid	30	632	51	43	62	46	42	48	85	30	48	632	100	BDL	139	21	BDL	20.6	139	67
Thiacloprid	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	5.2	BDL	BDL	BDL	5.2	33

Diazinon	0.2	0.9	BDL	BDL	BDL	0.35	BDL	BDL	0.5	BDL	BDL	0.9	44	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Dichlorvos	BDL	4.9	BDL	BDL	BDL	BDL	BDL	BDL	4.9	BDL	BDL	4.9	22	4.9	BDL	BDL	BDL	BDL	4.9	33
Dimethoate	1.0	1.4	1.3	BDL	BDL	BDL	BDL	1.4	1.7	BDL	1.0	1.7	56	BDL	BDL	BDL	BDL	BDL	BDL	0
Tebufenozide	1.4	0.4	1.5	6.4	1.3	1.2	1.9	0.4	1.7	0.4	1.4	6.4	100	BDL	BDL	BDL	BDL	BDL	BDL	0
Cyproconazole	1.0	0.6	0.6	0.5	0.1	0.1	3.3	0.7	0.7	0.1	0.6	3.3	100	0.1	0.7	BDL	BDL	0.1	0.7	67
Difenoconazole	BDL	0.8	3.6	1.9	BDL	BDL	2.7	0.2	2.4	BDL	0.8	3.6	67	BDL	1.4	BDL	BDL	BDL	1.4	33
Propiconazole	5.4	4.8	11	5.0	7.9	4.6	7.9	4.4	7.6	4.4	5.4	11	100	BDL	4.8	1.5	BDL	1.5	4.8	67
Tebuconazole	14	14	53	30	14	27	25	23	13	13	23	53	100	BDL	BDL	29	BDL	BDL	29	33
Triadimenol	17	11	22	16	10	13	21	13	12	11	13	22	100	0.4	9.3	6.8	0.4	6.8	9.3	100
Triazophos	BDL	BDL	6.8	0.3	BDL	0.3	BDL	BDL	0.3	BDL	BDL	6.8	44	BDL	0.3	BDL	BDL	BDL	0.3	33
Tricyclazole	14	12	19	42	6.4	13	17	13	12	6.4	13	42	100	BDL	18	8.8	BDL	8.8	18	67
Azoxystrobin	6.4	6.8	5.7	4.6	8.4	11	7.9	9.5	14	4.6	7.9	14	100	BDL	30	7.8	BDL	7.8	30	67
Prochloraz	0.4	BDL	0.4	0.4	BDL	BDL	0.4	0.4	0.4	BDL	0.4	0.4	67	BDL	0.4	BDL	BDL	BDL	0.4	33
Pyrimethanil	1.8	0.4	8.0	3.6	0.4	2.8	4.3	2.4	2.0	0.4	2.4	8.0	100	BDL	BDL	0.4	BDL	BDL	0.4	33
Carbendazim	153	336	513	582	40	312	366	575	468	40	366	582	100	BDL	219	209	BDL	209	219	67
Thiophanate-methyl	BDL	BDL	BDL	20	BDL	BDL	BDL	BDL	2.2	BDL	BDL	20	22	BDL	15	2.2	BDL	2.2	15	67
Boscalid	BDL	3.3	4.6	7.4	4.7	5.4	BDL	BDL	6.0	BDL	4.6	7.4	67	BDL	BDL	2.1	BDL	BDL	2.1	33
Dimethomorph	14	24	9.6	12	40	85	24	26	44	9.6	24	86	100	BDL	74	32	BDL	32	74	67
Metalaxyl	1.2	2.3	5.1	2.8	4.8	4.8	2.2	4.5	6.8	1.2	4.5	6.8	100	BDL	1.6	3.3	BDL	1.6	3.3	67
Isoprothiolane	13	4.9	4.9	5.5	1.2	4.9	5.8	6.9	3.9	1.2	4.9	13	100	BDL	19	2.8	BDL	2.8	19	67