

## Supplementary Information

### Development of a multi-residue method for 58 pesticides in soil using QuEChERS and gas chromatography-tandem mass spectrometry

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#### Table lists:

Table S 1. Physicochemical properties of different soil samples for the assessment of the method feasibility.

Table S 2. Recoveries and RSD of the comparisons between different buffers in soil samples.

Table S 3. Mean recoveries, RSD and ME of the comparison between different clean-up materials in soil samples.

Table S 4. Recovery data for pesticides from different provinces of soil fortified at 5  $\mu\text{g kg}^{-1}$ .

Table S 5. Recovery data for pesticides from different provinces of soil fortified at 50  $\mu\text{g kg}^{-1}$ .

Table S 6. Pesticides residues detected in real soil samples.

Table S 1. Physicochemical properties of different soil samples for the assessment of the method feasibility.

Samples	PH	Organic matter (%)	Sand (%)	Clay (%)
1	6.7	4.2	37.6	34.2
2	7.1	5.0	39.1	32.8
3	6.8	5.3	35.1	35.1
4	6.8	6.1	43.2	26.8
5	6.7	4.7	30.5	30.1
6	6.5	4.9	25.3	33.9
7	5.3	6.9	13.6	40.0
8	5.7	6.0	20.4	23.4
9	6.2	7.1	26.5	25.8
10	6.7	4.7	30.2	13.5
11	7.4	5.3	40.1	21.3
12	7.0	5.1	35.5	22.5
13	6.9	4.9	29.8	24.8
14	7.1	4.2	37.5	23.6
15	7.3	5.1	25.2	29.1
16	6.3	5.6	28.6	39.5
Black sample*	7.3	4.4	24.1	27.2

\*Properties of soil used in method development.

Table S 2. Recoveries and RSD of the comparisons between different buffers in soil samples.

Pesticides	No buffer		AOAC		EN	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
Dichlorvos	48	5	72	19	67	6
Isoprocarb	89	1	109	2	102	1
Atrazine-desethyl	93	2	111	3	106	2
Phorate	74	6	96	1	92	3
HCH-alpha	81	3	97	4	91	2
Atrazine	96	1	109	4	101	2
HCH-beta	80	1	102	1	94	3
HCH-gamma	79	1	101	1	95	2
Quintozene	59	8	92	10	82	6
Terbufos	63	3	101	1	98	2
Pyrimethanil	80	4	104	6	95	6
HCH-delta	75	3	103	3	92	2
Chlorothalonil	63	3	84	17	73	3
Acetochlor	101	5	105	1	99	2
Parathion-methyl	86	6	106	6	107	4
Alachlor	94	5	110	3	103	1
Phorate-sulfoxide	92	8	97	4	80	1
Malathion	84	4	110	7	108	1
Phorate-sulfone	97	2	117	5.6	109	1
Chlorpyrifos	68	9	101	4.9	95	3
Parathion	77	8	111	13	110	3
Dicofol	68	6	102	8	101	2
Triadimefon	96	8	114	5	110	2
Isocarbophos	97	5	121	12	123	3
Pendimethalin	71	4	114	12	113	4
Fipronil Sulfide	73	5	119	9	121	2
Fipronil	84	15	121	6	121	5
Procymidone	87	15	107	16	100	1
o,p'-DDE	62	10	95	2	88	4
Paclobutrazol	83	8	121	6	117	7

Endosulfan- $\alpha$	65	5	95	8	100	7
Butachlor	71	6	110	6	106	2
Hexaconazole	78	6	104	2	104	4
Isoprothiolane	82	2	108	2	107	2
Profenofos	69	4.8	103	3	107	2
Uniconazole	70	7	120	6	118	6
p,p'-DDE	61	8	97	2	89	3
Buprofezin	78	14	103	1	120	7
Fipronil Sulfone	84	7	108	9	115	6
Endosulfan- $\beta$	71	2	98	7	97	5
o,p'-DDT	62	4	92	5	84	10
Triazophos	79	3	115	8	109	4
Endosulfan sulfate	72	1	109	3	102	2
p,p'-DDT	59	8	93	7	79	8
Propiconazole	76	2	105	2	101	2
Tebuconazole	80	3	106	2	111	2
Propargite	56	3	117	8	82	3
Epoxiconazole	76	3	110	3	109	3
Iprodione	76	8	119	5	104	15
Bifenthrin	73	11	107	5	101	1
Fenpropathrin	58	4	105	3	99	4
Cyhalothrin	61	10	112	3.9	115	5
Spirodiclofen	84	5	119	15	108	8
Pyridaben	78	5	113	10	111	5
Cyfluthrin	79	7	107	11	108	11
Cypermethrin	67	12	105	5	101	9
Fenvalerate	61	8	110	4	98	3
Difenoconazole	73	1	110	5	118	6

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Table S 3. Mean recoveries, RSD and ME of the comparison between different clean-up materials in soil samples.

Pesticides	PSA & C18			PSA			C18		
	Mean	%RSD	%ME	Mean	%RSD	%ME	Mean	%RSD	%ME
Dichlorvos	78	22	-24	85	13	-14	66	28	-22
Isoprocarb	88	17	10	102	1	24	94	4	43
Atrazine-desethyl	81	14	-5	103	4	29	103	6	20
Phorate	85	19	26	83	1	195	71	19	160
HCH-alpha	81	15	-32	86	2	-9	79	10	-10
Atrazine	103	5	-7	97	4	27	93	1	19
HCH-beta	97	5	-52	94	3	-41	96	1	-41
HCH-gamma	93	2	-11	93	1	9	93	4	10
Quintozene	80	5	-25	94	18	2	73	8	1
Terbufos	108	5	-10	92	5	229	74	12	185
Pyrimethanil	87	12	1	101	6	40	87	4	25
HCH-delta	95	4	0	91	1	-43	85	3	-44
Chlorothalonil	81	14	-39	76	12	-8	72	4	6
Acetochlor	86	7	36	94	1	61	92	7	48
Parathion-methyl	101	8	8	105	8	123	91	8	110
Alachlor	96	8	21	96	1	27	94	4	18
Phorate-sulfoxide	99	3	69	98	4	81	100	6	71
Malathion	99	6	106	102	8	147	97	6	118
Phorate-sulfone	103	3	-10	107	4	0	100	4	-5
Chlorpyrifos	94	4	31	95	1	39	97	4	32
Parathion	97	7	15	106	4	76	91	8	62
Dicofol	86	5	12	126	21	19	105	3	-11
Triadimefon	109	8	33	103	1	50	98	10	37
Isocarbophos	118	12	154	108	7	367	99	3	278
Pendimethalin	101	11	9	105	3	55	78	3	45
Fipronil Sulfide	106	3	16	104	5	39	99	4	27
Fipronil	118	7	9	116	10	94	100	13	61
Procymidone	82	5	-8	104	4	4	89	3	-7
o,p'-DDE	84	3	-6	88	2	-1	82	4	-6
Paclobutrazol	119	6	136	113	7	247	104	4	174

Endosulfan- $\alpha$	87	10	-2	108	18	-2	87	11	-8
Butachlor	99	7	43	100	7	107	90	4	82
Hexaconazole	104	5	21	126	18	180	79	10	141
Isoprothiolane	99	6	86	92	3	234	95	5	162
Profenofos	106	2	27	94	7	321	91	1	218
Uniconazole	100	10	77	103	10	251	89	1	189
p,p'-DDE	87	3	-9	89	3	-5	85	5	-9
Buprofezin	100	13	54	109	9	164	91	12	129
Fipronil Sulfone	115	10	30	122	10	72	110	12	40
Endosulfan- $\beta$	97	7	-2	86	9	1	80	8	1
o,p'-DDT	91	4	2	82	8	16	85	2	0
Triazophos	113	14	56	111	7	103	96	7	77
Endosulfan sulfate	91	12	26	99	5	42	98	4	33
p,p'-DDT	84	13	15	75	15	34	75	3	22
Propiconazole	89	3	128	99	2	249	99	2	189
Tebuconazole	84	22	91	93	3	393	98	3	286
Propargite	100	9	179	97	13	426	103	6	420
Epoxiconazole	102	14	115	115	5	311	94	4	243
Iprodione	97	13	16	82	13	262	96	7	269
Bifenthrin	88	12	198	96	3	141	89	3	103
Fenpropathrin	83	11	30	97	12	118	87	3	89
Cyhalothrin	119	12	57	113	6	230	122	17	178
Spirodiclofen	110	9	26	97	16	179	80	14	153
Pyridaben	104	6	198	99	8	321	93	6	242
Cyfluthrin	94	17	3	122	9	146	92	15	154
Cypermethrin	110	13	14	96	6	216	114	3	199
Fenvalerate	104	13	41	107	4	263	100	4	187
Difenoconazole	111	7	16	123	17	222	119	24	162

Table S 4. Recovery data for pesticides from different provinces of soil fortified at 5  $\mu\text{g kg}^{-1}$ .

Pesticides	Shandong		Jiangsu		Liaoning	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
Dichlorvos	68	7	67	17	60	11
Isoproc carb	92	5	97	11	90	10
Atrazine-desethyl	91	4	97	1	87	4
Phorate	62	9	61	19	64	10
HCH-alpha	63	6	67	19	70	7
Atrazine	72	3	106	13	103	2
HCH-beta	83	4	82	5	102	3
HCH-gamma	71	2	73	16	79	8
Quintozene	49	10	60	13	118	16
Terbufos	66	6	66	8	70	8
Pyrimethanil	94	9	101	7	79	11
HCH-delta	85	5	87	3	92	4
Chlorothalonil	81	16	107	14	119	3
Acetochlor	70	4	74	4	91	3
Parathion-methyl	93	4	100	6	91	5
Alachlor	90	1	96	5	92	1
Phorate-sulfoxide	94	10	102	5	99	7
Malathion	86	6	92	6	87	4
Phorate-sulfone	87	2	85	15	86	4
Chlorpyrifos	83	5	82	4	91	3
Parathion	75	3	69	14	79	16
Dicofol	56	4	55	6	56	4
Triadimefon	88	2	99	1	92	6
Isocarbophos	96	4	111	11	98	9
Pendimethalin	88	7	71	5	79	19
Fipronil Sulfide	97	3	107	7	93	2
Fipronil	113	1	116	10	117	3
Procymidone	117	20	118	13	85	23
o,p'-DDE	77	3	71	8	88	2
Paclobutrazol	65	1	65	1	65	1
Endosulfan- $\alpha$	99	11	89	8	105	12

Butachlor	89	6	100	16	95	5
Hexaconazole	90	4	110	10	95	14
Isoprothiolane	94	4	117	5	105	8
Profenofos	106	8	108	6	113	8
Uniconazole	94	8	103	9	90	6
p,p'-DDE	63	6	64	15	91	10
Buprofezin	110	10	114	16	110	12
Fipronil Sulfone	126	2	125	20	125	17
Endosulfan- $\beta$	100	8	89	6	110	13
o,p'-DDT	94	3	110	13	104	3
Triazophos	89	7	101	13	96	9
Endosulfan sulfate	92	7	91	6	97	4
p,p'-DDT	64	10	62	5	69	9
Propiconazole	95	3	98	9	97	10
Tebuconazole	77	5	115	3	73	8
Propargite	81	17	99	15	90	5
Epoxiconazole	78	5	90	3	85	10
Iprodione	114	16	110	12	100	17
Bifenthrin	85	5	85	8	94	4
Fenpropathrin	91	14	76	12	80	9
Cyhalothrin	78	5	82	8	85	6
Spirodiclofen	85	17	107	5	87	20
Pyridaben	80	8	82	9	103	2
Cyfluthrin	114	18	112	16	114	2
Cypermethrin	117	2	96	10	111	10
Fenvalerate	106	13	105	16	119	12
Difenoconazole	127	3	123	4	130	10

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Table S 5. Recovery data for pesticides from different provinces of soil fortified at 50  $\mu\text{g kg}^{-1}$ .

Pesticides	Shandong		Jiangsu		Liaoning	
	Mean	%RSD	Mean	%RSD	Mean	%RSD
Dichlorvos	61	17	66	10	69	8
Isoprocarb	79	5	82	4	87	8
Atrazine-desethyl	89	2	91	3	90	3
Phorate	90	8	100	5	98	24
HCH-alpha	84	12	76	4	78	11
Atrazine	85	2	88	1	88	1
HCH-beta	77	3	80	2	89	3
HCH-gamma	84	9	75	8	80	5
Quintozene	86	5	88	8	79	16
Terbufos	84	6	73	7	83	20
Pyrimethanil	76	3	78	5	78	8
HCH-delta	76	3	79	2	86	6
Chlorothalonil	76	9	68	10	111	8
Acetochlor	77	2	80	1	86	4
Parathion-methyl	68	3	74	6	78	10
Alachlor	81	2	84	2	86	2
Phorate-sulfoxide	75	4	77	1	76	9
Malathion	72	5	74	3	80	11
Phorate-sulfone	65	8	69	3	85	5
Chlorpyrifos	72	11	672	2	81	4
Parathion	79	4	75	2	74	12
Dicofol	70	18	68	2	67	36
Triadimefon	87	2	88	1	88	3
Isocarbophos	71	12	75	3	75	13
Pendimethalin	75	7	77	4	77	9
Fipronil Sulfide	94	5	95	2	97	5
Fipronil	120	8	120	1	117	7
Procymidone	90	1	88	7	92	3
o,p'-DDE	78	4	75	1	85	2
Paclobutrazol	87	2	87	2	95	4
Endosulfan- $\alpha$	72	9	73	2	81	5



Butachlor	82	6	77	3	79	8
Hexaconazole	76	4	78	2	81	9
Isoprothiolane	77	6	77	3	81	11
Profenofos	81	11	76	8	76	19
Uniconazole	77	7	78	6	77	10
p,p'-DDE	74	3	78	5	83	2
Buprofezin	74	5	81	1	78	7
Fipronil Sulfone	119	5	128	2	119	6
Endosulfan- $\beta$	77	5	77	3	94	1
o,p'-DDT	84	4	98	2	122	2
Triazophos	78	11	79	4	72	18
Endosulfan sulfate	79	4	81	1	86	6
p,p'-DDT	78	3	79	14	88	12
Propiconazole	92	2	91	8	87	5
Tebuconazole	85	6	86	3	83	9
Propargite	88	8	72	2	78	11
Epoxiconazole	74	8	79	3	82	12
Iprodione	121	14	119	13	103	26
Bifenthrin	83	7	78	3	83	4
Fenpropathrin	82	15	76	6	81	5
Cyhalothrin	70	10	72	2	89	5
Spirodiclofen	86	18	83	2	78	1
Pyridaben	71	13	84	4	108	9
Cyfluthrin	89	20	83	4	90	16
Cypermethrin	78	10	85	7	101	2
Fenvalerate	91	18	101	15	114	12
Difenoconazole	124	1	123	12	117	6

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Table S 6. Pesticides residues detected in real soil samples ( $\mu\text{g kg}^{-1}$ ).

Pesticides	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6		Sample 7		Sample 8		
	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S	
Isoprocarb						0.51											
Atrazine	0.26		0.40	0.62	0.52	0.50			2.5	3.2	2.6	2.7	1.0				2.8
HCH-beta									7.1	11.0							
Terbufos			3.6														
Acetochlor	1.9	2.2	2.0	0.70	2.0	0.44			2.2	2.6	3.8	1.1	1.9	0.53	2.0	1.1	
Phorate Sulfone	12	13															
Chlorpyrifos	25	23	4.0	2.3	4.2	2.6						0.56					
Dicofol									4.4	4.0	5.0						
Pendimethalin	3.9	1.4	4.3	0.5			4.2	0.73	11	20							
Procymidone				4.7	16	14											
o,p'-DDE									3.1	3.2	2.2						
p,p'-DDE	0.72	0.71	0.74	1.3	0.62	0.70	1.1	1.2	99	76	1.3	1.4	4.6	5.3	0.64	1.8	
Endosulfan- $\beta$	3.4	2.7															
o,p'-DDT									11	16	5.0		3.7	3.7			
Endosulfan sulfate	4.2	3.0			2.6		2.7				2.7						
p,p'-DDT									32	15							
Tebuconazole									5.8	4.3	5.5						
Cyhalothrin	41		4.3						4.6		4.6					21	

Pyridaben 4.8

Difenoconazole 5.0 5.0 5.0

Table S 6. Pesticides residues detected in real soil samples ( $\mu\text{g kg}^{-1}$ ). (cotinued)

Pesticides	Sample 9		Sample 10		Sample 11		Sample 12		Sample 13		Sample 14		Sample 15		Sample 16	
	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S	Q	S
phorate									2.3	5.2						
HCH-alpha		0.11									1.6	1.3				
Atrazine		1.3											0.71		3.6	2.6
HCH-beta	2.2		2.3	1.8	2.1	1.3	3.6	2.5	4.0	3.8	6.6	4.6	2.6	2.2	2.3	
PCNB									$4.1 \times 10^2$	$4.2 \times 10^2$	9.7	11				
pyrimethanil					27	29	4.2	3.0	21	19	8.8	11				
HCH-delta											2.7	1.8				
Acetochlor	5.2	6.4	4.7	4.0	1.9	2.6	1.8	2.6			1.9	1.4	2.8	2.2	2.1	1.3
Phorate Sulfone	5.1	12							28	26	$1.4 \times 10^2$	$1.3 \times 10^2$				
Chlorpyrifos	12	15							43	44	$2.6 \times 10^2$	$2.5 \times 10^2$				
Parathion											4.1	4.6				
Dicofol			3.8	3.0	3.9	3.7	4.8	4.5			3.7	1.5	3.7		3.7	
Pendimethalin			7.9	7.0			4.3	2.1			6.8	5.6	3.9	3.1		
Fipronil Sulfide											6.0	6.0				
Fipronil											9.0	9.6				
Procymidone					27	21	26	21	56	52	17	16				

o,p'-DDE	2.1		2.0	2.8	2.1	2.8	2.4	3.1	2.0		2.0					
Paclobutrazol					3.5	3.4	3.0	2.0			3.0	1.3				
Endosulfan- $\alpha$									5.0	6.6	4.3	4.4				
Hexaconazole	5.5		36													
Profenofos					54	58	4.5	4.7								
p,p'-DDE	3.7	6.8	10	20	13	19	37	51	2.5	3.0	2.7	4.7	1.1	4.0	1.7	3.4
Fipronil Sulfone											5.0	1.8				
Endosulfan- $\beta$									80	77	36	40				
o,p'-DDT	4.3	5.9	5.2	6.7	3.2	6.0	30	43	3.0	1.1	3.0	2.4	3.0	1.3	4.2	2.0
Endosulfan sulfate					22	21			$2.8 \times 10^2$	$2.7 \times 10^2$	$1.3 \times 10^2$	$1.5 \times 10^2$	2.7	1.4	2.7	1.3
p,p'-DDT	3.4	3.6	3.7	5.3	4.3	5.4	27	25	3.0	2.3	3.8	2.7			3.5	2.1
Propiconazole					4.9	7.6	6.0	14	4.7	4.2	14	13				
Tebuconazole	5.2								21	18	28	26				
Bifenthrin					4.0	1.0			16	16	5.0	5.0			4.0	
Cyhalothrin					4.6				4.6	2.7	11	10				
Pyridaben							6.7		21	9.7	48	42	6.6	8.0	8.5	14
Fenvalerate					5.0	6.1	5.0	4.0								
Difenoconazole					33	23	12	11	40	26	56	53				

Blank regions were not detected.

Q:QuEChE S:shacking.