

Residue analysis of sixty pesticides in red swamp crayfish using QuEChERS with high-performance liquid chromatography-tandem mass spectrometry

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Supporting Information:

Table S1-S5, Figure S1-S3.

Table S1. MRM parameters for sixty pesticides analysis by HPLC-MS/MS.

Compound	Gradient elution/ t _R (min)	Isocratic elution/ t _R (min)	Quant MRM (m/z)	Qual MRM (m/z)	Fragmentor (V)	Collision energy (V)
Acetamiprid	9.17	0.92	223.2/126.0	223.2/56.0	120	15, 15
Anilofos	14.42	1.99	368.1/125.0	368.1/171.0	100	15, 30
Atrazine	11.75	1.22	216.0/174.2	216.0/132	120	15, 20
Azoxystrobin	13.17	1.33	404.0/372.0	404.0/344.1	120	10, 15
Bentazone	16.20	3.51	240.3/162.1	240.3/147.1	80	10, 20
Boscalid	13.32	1.50	343.2/307.2	343.2/271.0	140	20, 35
Buprofezin	14.20	2.79	306.2/116.0	306.2/201.0	120	10, 15
Butachlor	16.00	3.47	312.2/238.1	312.2/162	80	10, 20
Carbendazim	7.33	0.86	192.1/160.1	192.1/132.1	80	15, 20
Carbofuran	11.43	1.09	222.3/165.1	222.3/123.1	120	5, 20
Carfentrazone-ethyl	14.12	1.77	412.0/346.0	412.0/366.0	135	20, 20
Chlorpyrifos	16.45	3.96	350.0/198.0	350.0/79.0	100	20, 35
Clodinafop	14.67	1.89	350.1/266.1	350.1/238.1	120	15, 20
Clodinafop-propargyl	13.46	1.59	310.0/127.0	310.0/153.0	135	45, 25
Clothianidin	8.37	0.94	250.2/169.1	250.2/132	80	10, 15
Cyhalofop-butyl	15.49	2.68	358.1/256.1	358.1/120.1	70	5, 25
Cyprodinil	12.55	1.76	226.0/93.0	226.0/108.0	120	40, 30
Difenoconazole	14.48	2.04	406.0/251.0	406.0/337.0	155	25, 15
Dinotefuran	7.13	1.01	203.0/73.1	203.0/58.2	80	20, 25
Epoxiconazole	13.26	1.46	330.1/121.1	330.1/141.1	120	20, 20
Fenoxaprop-p	13.34	1.40	334.1/288.1	334.1/244.1	140	15, 15
Fenoxaprop-p-ethyl	15.56	2.66	362.2/288.1	362.2/244.2	100	15, 20
Florasulam	11.36	0.99	360.0/129.0	360.0/192.0	135	20, 20
Flutriafol	11.91	1.05	302.1/123.1	302.1/170.1	120	22, 15
Halosulfuron-methyl	13.09	1.39	434.8/181.9	434.8/402.7	120	15, 4
Hexaconazole	13.51	1.73	314.1/70.1	314.1/158.9	120	20, 35
Hymexazol	1.00	0.92	100.1/44.2	100.1/54.1	100	15, 10
Imidacloprid	8.78	0.90	256.1/175.1	256.1/209.1	80	10, 10
Isoprocab	11.97	1.20	194.1/95.0	194.1/137.1	80	20, 5
Isoprothiolane	13.60	1.67	291.1/189.1	291.1/231.1	80	20, 5
Isoproturon	11.87	1.17	207.2/72.0	207.2/165.1	120	15, 15

Kresoxim-methyl	14.15	1.81	314.0/222.1	314.0/193.9	100	8, 30
Mefenacet	13.28	1.50	299.1/148.2	299.1/120.0	90	4, 10
Metalaxyl-M	11.81	1.17	280.2/160.1	280.2/192.2	100	20, 10
Methomyl	7.42	0.91	163.2/88.1	163.2/106.1	80	10, 5
Metolachlor	13.66	1.78	284.2/176.4	284.2/253.2	95	12, 12
Nicosulfuron	10.51	4.18	411.0/182.0	411.0/213.0	120	19, 19
Nitenpyram	7.66	0.83	271.1/224.1	271.1/237.1	100	15, 15
Penoxsulam	12.30	1.07	484.0/195.1	484.0/164	150	30, 40
Picoxystrobin	14.48	1.82	368.1/145.0	368.1/205.0	80	12, 4
Pirimicarb	7.86	1.02	239.2/72.0	239.2/182.2	120	20, 15
Pretilachlor	15.22	2.68	312.2/252.2	312.2/176.2	100	10, 15
Prochloraz	12.79	1.53	376.7/309.0	376.7/267.0	85	8, 10
Prometryn	11.23	1.32	242.2/158.1	242.2/200.1	120	20, 20
Propamocarb	0.99	0.77	189.2/102.1	189.2/74.1	100	15, 30
Propiconazole	13.95	1.87	342.2/158.9	342.2/69.1	70	30, 20
Pymetrozine	1.19	0.81	218.1/105.1	218.1/78.0	100	20, 40
Pyraclostrobine	14.81	2.17	387.8/163.1	387.8/149.0	90	20, 30
Pyrazosulfuron-ethyl	12.95	1.32	415.0/182.0	415.0/139.0	102	15, 15
Pyridaben	17.06	5.90	365.1/147.1	365.1/309.1	100	20, 20
Pyrimethanil	11.03	1.42	200.2/107.0	200.2/183.1	120	25, 25
Tebuconazole	13.44	1.59	308.2/70.0	308.2/125.0	100	25, 25
Thiabendazole	7.60	0.86	202.1/175.1	202.1/131	145	25, 30
Thiamethoxam	7.93	0.94	292.1/211.2	292.1/181.1	80	10, 20
Thifluzamide	14.46	2.10	529.0/488.9	529.0/168	160	30, 25
Triazophos	13.83	1.59	314.1/162.1	314.1/97.0	100	20, 35
Tricyclazole	9.31	0.96	190.0/163.0	190.0/136.0	145	25, 30
Trifloxystrobin	15.25	2.43	409.3/186.1	409.3/206.2	120	15, 10
Trifloxystrobin acid	13.88	1.53	395.1/186.0	395.1/145.0	100	16, 52
Trifluralin	14.69	4.68	336.0/205.7	336.0/235.7	100	20, 10
TPP	14.54	2.00	327.1/215.1	327.1/153.1	135	30, 20

Table S2. % Percentage pesticides out of 60 with satisfactory recoveries (70% -120%) and RSDs ($\leq 20\%$) (n=3) using different cleanup sorbents: (a) No clean up; (b) 50 mg PSA; (c) 50 mg PSA + 150 mg MgSO₄; (d) 50 mg PSA + 50 mg C18 + 150 mg MgSO₄; (e) 50 mg PSA + 5 mg MWCNTs + 150 mg MgSO₄.

	% Whole crayfish					% Crayfish meat				
	a	b	c	d	e	a	b	c	d	e
Satisfactory recovery	88	88	83	80	73	90	92	82	87	77
RSD	88	92	92	93	92	88	92	90	87	93

- 12 Table S3. Lowest calibrated level (LCL), signal to noise (S/N), limit of detection (LOD), limit of quantitation (LOQ) and ion ratios for the
 13 selected pesticides.

Pesticide	LCL (ng/g)	S/N	LOD (ng/g)	LOQ (ng/g)	Ion ratio	Pesticide	LCL (ng/g)	S/N	LOD (ng/g)	LOQ (ng/g)	Ion ratio
Propamocarb	5	4	3.8	12.5	2.7	Mefenacet	5	2	6.2	25	12
Hymexazol	5	12	1.3	4.2	45	Epoxiconazole	5	29	0.5	1.7	3.2
Pymetrozine	5	18	0.8	2.8	10	Boscalid	5	6	2.5	8.3	2.4
Dinotefuran	5	12	1.3	4.2	1.1	Fenoxaprop-p	5	2	9.6	25	16
Carbendazim	5	7	2.1	7.1	13	Tebuconazole	5	11	1.4	4.5	2.0
Nitenpyram	5	4	3.8	12.5	5.7	Clodinafop-propargyl	5	6	2.7	8.3	2.2
Thiabendazole	5	8	1.8	6.3	1.8	Hexaconazole	5	22	0.7	2.3	8.5
Methomyl	5	9	1.6	5.6	2.7	Isoprothiolane	5	9	1.8	5.5	1.0
Pirimicarb	5	41	0.4	1.2	1.6	Metolachlor	5	19	0.8	2.6	84
Thiamethoxam	5	41	0.4	1.2	1.8	Triazophos	5	23	0.6	2.2	6.0
Clothianidin	5	6	2.5	8.3	1.5	Trifloxystrobin acid	5	16	0.9	3.1	1.8
Imidacloprid	5	18	0.8	2.8	1.0	Propiconazole	5	27	0.6	1.8	1.7
Acetamiprid	5	16	0.9	3.2	2.6	Thifluzamide	5	2	6.4	25	1.0
Tricyclazole	5	13	1.1	3.8	1.1	Buprofezin	5	37	0.4	1.4	3.9
Nicosulfuron	-	-	-	-	-	Carfentrazone-ethyl	5	17	0.9	2.9	2.5
Pyrimethanil	5	14	1.0	3.6	1.5	Kresoxim-methyl	5	6	2.4	8.3	1.0
Carbofuran	5	10	1.4	5	1.5	Picoxystrobin	5	6	2.6	8.3	4.2
Prometryn	5	35	0.4	1.4	2.3	Difenoconazole	5	7	2.2	7.1	2.1
Florasulam	5	14	1.1	3.6	45	Anilofos	5	7	2.0	7.1	1.2
Flutriafol	5	17	0.9	2.9	588	Clodinafop	5	3	4.8	16	3.6
Atrazine	5	22	0.7	2.3	4.9	Trifluralin	-	-	-	-	-
Metalaxyl-M	5	22	0.7	2.3	1.1	Pyraclostrobin	5	11	1.3	4.5	2.6
Isoproturon	5	37	0.4	1.4	10	Pretilachlor	5	5	2.8	10	23

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Isoprocab	5	8	1.8	6.3	3.4	Trifloxystrobin	5	13	1.2	3.8	3.0
Penoxsulam	5	21	0.7	2.4	4.5	Fenoxaprop-p-ethyl	5	19	0.8	2.6	11
Cyprodinil	5	16	0.9	3.1	10	Cyhalofop-butyl	5	1	30.0	50	2.0
Prochloraz	5	10	1.6	5.0	3.0	Butachlor	5	14	1.1	3.5	4.5
Pyrazosulfuron-ethyl	5	9	1.6	5.6	8.6	Bentazone	5	14	1.1	3.5	1.7
Azoxystrobin	5	13	1.2	3.8	29	Chlorpyrifos	-	-	-	-	-
Halosulfuron-methyl	5	20	0.7	2.5	3.2	Pyridaben	5	12	1.3	4.2	5.0

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Table S4. % Fortified recoveries and (RSDs) for 60 pesticides in isocratic elution (n=5).

	Whole crayfish			Crayfish meat		
Pesticide	% Recoveries (% RSD)			% Recoveries (% RSD)		
	10 ng/g	50 ng/g	100 ng/g	10 ng/g	50 ng/g	100 ng/g
Propamocarb	78(13)	48 (2)	71(2)	49 (5)	93(12)	74(3)
Nitenpyram	88(32)	61(6)	98(9)	97(35)	98(13)	94(12)
Carbendazim	103(11)	85(4)	98(12)	114(20)	90(7)	111(13)
Pymetrozine	85(4)	46 (5)	78(7)	91(21)	85(6)	77(5)
Thiabendazole	83(11)	80(3)	107(9)	89(4)	99(12)	76(5)
Dinotefuran	91(14)	81(19)	93(11)	84(10)	98(13)	94(12)
Hymexazol	100(6)	78(7)	87(15)	81(15)	77(13)	88(11)
Thiamethoxam	96(19)	102(16)	118(6)	64 (32)	82(12)	79(9)
Methomyl	101(14)	100(10)	94(12)	79(8)	75(7)	105(10)
Clothianidin	81(27)	102(13)	105(25)	97(13)	84(12)	98(7)
Acetamiprid	120(35)	93(6)	124(16)	74(7)	91(13)	76(3)
Imidacloprid	126 (31)	113(24)	108(16)	77(19)	74(10)	103(8)
Tricyclazole	95(26)	89(6)	116(13)	95(11)	97(13)	76(5)
Florasulam	97(9)	77(9)	109(11)	70(8)	80(9)	103(7)
Pirimicarb	96(15)	82(3)	107(10)	99(1)	87(3)	83(7)
Penoxsulam	94(9)	78(4)	106(10)	99(13)	91(12)	105(6)
Flutriafol	95(6)	90(5)	111(6)	102(6)	98(4)	86(7)
Carbofuran	91(22)	88(6)	119(13)	109(11)	87(11)	108(7)
Metalaxyl-M	99(15)	85(5)	115(3)	106(11)	97(12)	114(6)
Isoproturon	98(11)	88(2)	111(5)	85(4)	102(13)	82(5)
Isoprocarb	91(16)	82(4)	115(9)	85(4)	94(12)	79(5)
Atrazine	103(13)	87(5)	106(9)	104(2)	105(13)	82(6)
Prometryn	103(12)	88(6)	114(3)	103(5)	104(10)	85(5)
Pyrazosulfuron-ethyl	91(14)	79(5)	112(9)	88(7)	87(10)	113(11)
Azoxystrobin	99(14)	85(4)	116(2)	113(10)	110(9)	85(5)
Pyrimethanil	99(9)	83(4)	111(2)	99(1)	90(3)	86(5)
Halosulfuron-methyl	99(12)	87(10)	111(10)	98(12)	99(12)	113(11)
Fenoxaprop-p	50 (17)	34 (4)	44 (8)	57 (14)	86(10)	103(8)
Epoxiconazole	98(9)	81(4)	112(4)	112(8)	100(2)	91(5)
Prochloraz	87(10)	84(7)	116(6)	98(7)	96(13)	88(9)
Boscalid	90(13)	87(5)	113(5)	89(11)	95(6)	87(6)
Mefenacet	98(21)	89(2)	105(7)	103(6)	106(9)	78(5)
Trifloxystrobin acid	80(17)	60 (3)	74(2)	98(6)	75(6)	87(8)
Clodinafop-propargyl	83(10)	85(8)	114(5)	99(11)	102(12)	92(7)
Tebuconazole	93(10)	80(6)	114(4)	100(4)	100(13)	82(5)
Triazophos	122 (29)	98(4)	102(4)	103(10)	106(9)	115(9)
Isoprothiolane	119(27)	110(4)	111(7)	93(9)	105(6)	78(4)
Thifluzamide	113(90)	92(20)	107(12)	96(30)	107(31)	93(19)
Cyprodinil	96(13)	86(7)	108(3)	101(2)	101(10)	86(6)
Hexaconazole	93(9)	92(4)	109(3)	103(6)	88(4)	83(4)
Carfentrazone-ethyl	102(12)	106(6)	116(4)	100(29)	125 (21)	114(7)
Metolachlor	114(27)	108(5)	107(6)	108(8)	110(7)	111(2)

Picoxystrobin	130(35)	114(4)	108(6)	88(9)	107(6)	85(6)
Kresoxim-methyl	97(10)	113(9)	111(5)	88(18)	95(9)	81(7)
Propiconazole	102(9)	86(4)	105(7)	106(6)	106(17)	85(5)
Clodinafop	104(23)	109(4)	106(3)	99(15)	93(5)	107(8)
Anilofos	115(23)	105(2)	118(4)	105(8)	107(8)	82(4)
Difenoconazole	93(12)	85(6)	112(4)	104(6)	88(2)	84(5)
Pyraclostrobin	93(35)	105(6)	111(7)	106(2)	103(9)	81(4)
Trifloxystrobin	125(46)	111(6)	119(14)	106(10)	101(10)	83(5)
Fenoxaprop-p-ethyl	93(22)	107(5)	119(8)	103(10)	90(9)	76(4)
Pretilachlor	104(23)	108(4)	119(8)	87(8)	96(10)	118(5)
Buprofezin	96(12)	84(4)	105(12)	100(1)	103(13)	84(5)
Cyhalofop-butyl	81(33)	99(15)	106(16)	159(59)	117(23)	108(9)
Butachlor	143(74)	117(18)	137(19)	104(14)	96(5)	78(6)
Bentazone	116(41)	102(13)	131(26)	98(17)	99(9)	88(7)
Chlorpyrifos	89(11)	95(11)	107(9)	87(4)	86(7)	104(13)
Nicosulfuron	44(26)	97(69)	103(47)	74(46)	83(43)	100(36)
Trifluralin	115(96)	57(21)	119(51)	68(19)	113(38)	98(10)
Pyridaben	88(11)	84(5)	103(12)	97(5)	97(12)	118(1)
TPP	77(14)	80(13)	87(8)	113(12)	105(8)	99(9)

Note: Recoveries of <70% and >120% and RSDs>20% (RSDs>30% for 10 ng/g spiking level) are in bold.

Table S5. % Matrix Effects (%ME) for whole crayfish and crayfish meat in gradient and isocratic elution conditions.

Pesticide	Gradient elution		Isocratic elution	
	whole crayfish	crayfish meat	whole crayfish	crayfish meat
Propamocarb	-27	-23	-69	-71
Pymetrozine	-79	-79	-75	-71
Dinotefuran	-20	-10	-88	-88
Carbendazim	4	32	-80	-73
Nitenpyram	6	21	-78	-72
Thiabendazole	8	30	-67	-60
Methomyl	-23	-5	-81	-87
Pirimicarb	-16	1	-42	-27
Thiamethoxam	-22	-11	-81	-83
Clothianidin	-22	-11	-67	-78
Imidacloprid	-17	-7	-66	-67
Acetamiprid	-26	-16	-45	-48
Tricyclazole	-26	-5	-50	-43
Nicosulfuron	11	45	-	-
Pyrimethanil	-28	-10	-20	-14
Prometryn	-22	-10	-17	-15
Carbofuran	-32	-10	-42	-47
Florasulam	-16	-5	-51	-62
Atrazine	-28	-9	-23	-17
Flutriafol	-16	-10	-26	1
Metalaxyl-M	-31	-8	-27	-16
Isoproturon	-29	-9	-27	-34
Isoprocarb	-29	-7	-33	-25
Penoxsulam	-13	12	-54	-39
Cyprodinil	-33	-8	-31	-13
Prochloraz	-51	-10	-32	49
Pyrazosulfuron-ethyl	-26	18	7	52
Azoxystrobin	-30	-6	-6	79
Halosulfuron-methyl	-23	3	2	98
Mefenacet	-28	-9	13	42
Epoxiconazole	-13	-3	17	69
Boscalid	-19	-2	-12	2
Fenoxaprop-p	93	120	143	247
Tebuconazole	-7	-10	14	49
Clodinafop-propargyl	-4	34	21	125
Hexaconazole	-12	-7	35	46
Isoprothiolane	-27	-29	9	12
Metolachlor	-16	-18	5	8
Triazophos	-21	-28	19	61
Trifloxystrobin acid	121	113	72	137
Propiconazole	-25	-17	37	51
Thifluzamide	-21	-16	-30	-38

Buprofezin	-18	-15	-10	-12
Carfentrazone-ethyl	-16	-43	-32	-20
Kresoxim-methyl	-39	-46	-33	-30
Picoxystrobin	-36	-58	-9	-9
Difenoconazole	-14	-11	33	43
Anilofos	-16	-37	27	13
Clodinafop	-25	-25	12	24
Pyraclostrobin	-34	-30	18	49
Pretilachlor	-27	-29	48	89
Trifloxystrobin	-37	-58	47	62
Fenoxaprop-p-ethyl	-39	-59	75	180
Cyhalofop-butyl	-84	-54	-44	-31
Butachlor	-35	-50	-12	-35
Bentazone	-27	-49	3	-12
Pyridaben	-5	-18	0	27
Chlorpyrifos	-	-	-13	-22
Hymexazol	-	-	-88	-92

Note: MEs were calculated using the equation: $\%ME = 100\% \times (\text{slope}_{\text{matrix}} / \text{slope}_{\text{MeCN}} - 1)$.

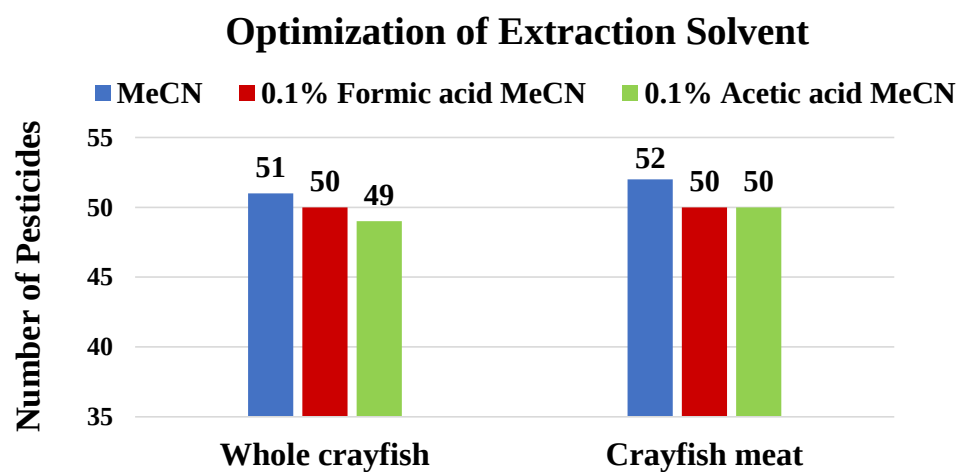


Figure S1. Comparison of different extraction solvents yielding satisfactory recovery (70–120%) and RSDs <20% for tested pesticides.

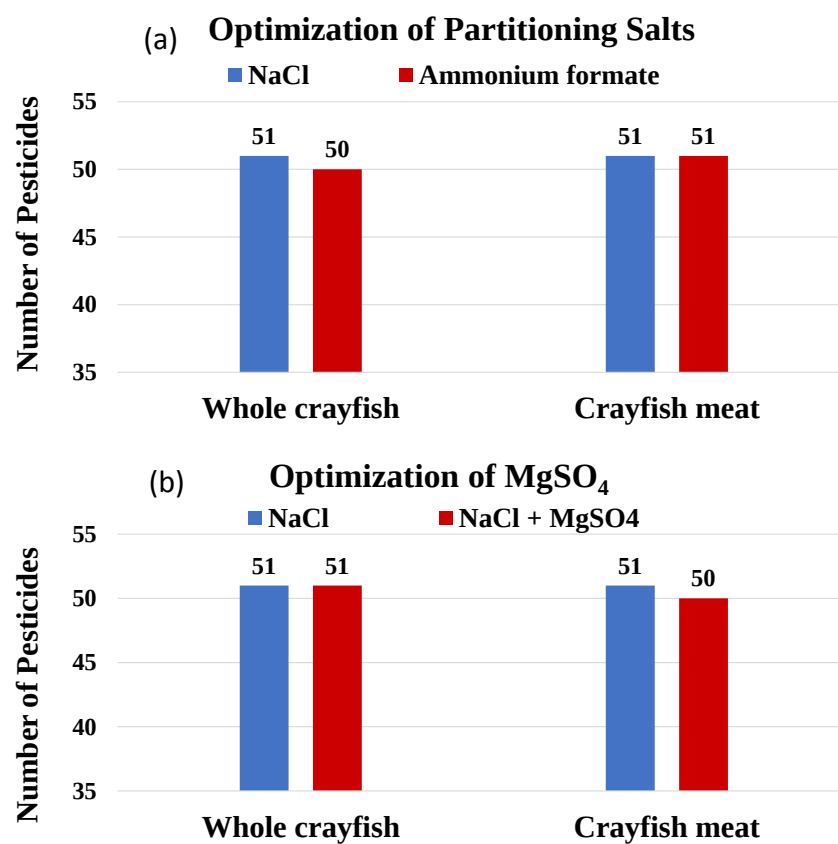


Figure S2. Comparison between NaCl and $\text{NH}_4\text{O}_2\text{CH}$ (a) and NaCl with or without MgSO_4 (b) to yield satisfactory recoveries and RSDs for tested pesticides

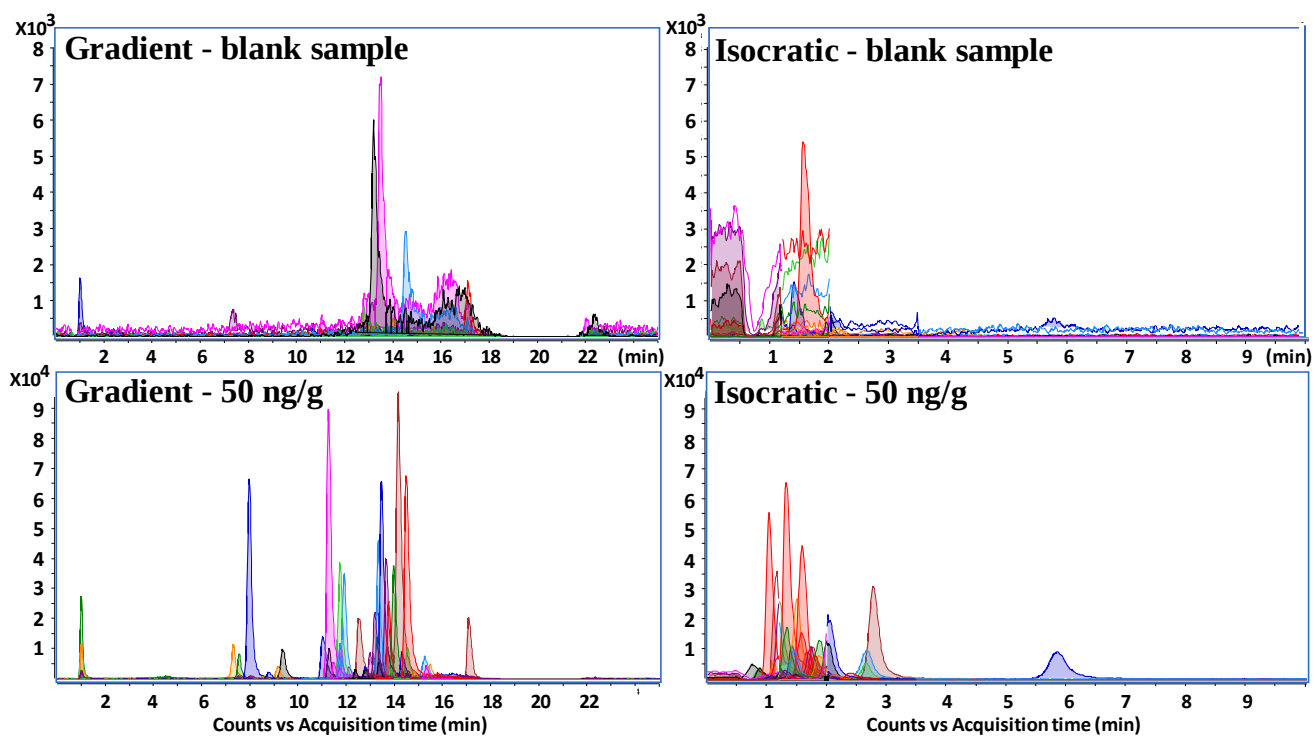


Figure S3. Typical MRM chromatograms of the 60 pesticides in crayfish at gradient and isocratic elution systems.