

Supplementary Materials

A critical comparison between an ultra-high-performance liquid chromatography triple quadrupole mass spectrometry (UHPLC-QqQ-MS) method and an enzyme assay for anti-cholinesterase pesticide residue detection in cereal matrices

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1. Tuning

Table S1. Analyte dependent parameters during tuning process.

Analyte	Precursor	Product	CE	Abundance
chlorpyrifos	349.9 [M+H] ⁺	96.7	40	6919790
	349.9 [M-H] ⁺	197.8	24	6455688
	351.9 [M-H] ⁻	199.9	20	5504219
	224.1 [M-H] ⁺	167.1	8	493497
	224.1 [M-H] ⁺	109	20	471592
bendiocarb	224.1 [M-H] ⁺	81	38	276557
	224.1 [M-H] ⁺	59.2	24	65669
	221.0 [M-H] ⁺	109	20	852331
	221.0 [M-H] ⁺	79	30	147101
dichlorvos	221.0 [M-H] ⁺	127	20	76516
	221.0 [M-H] ⁺	94.7	32	2118

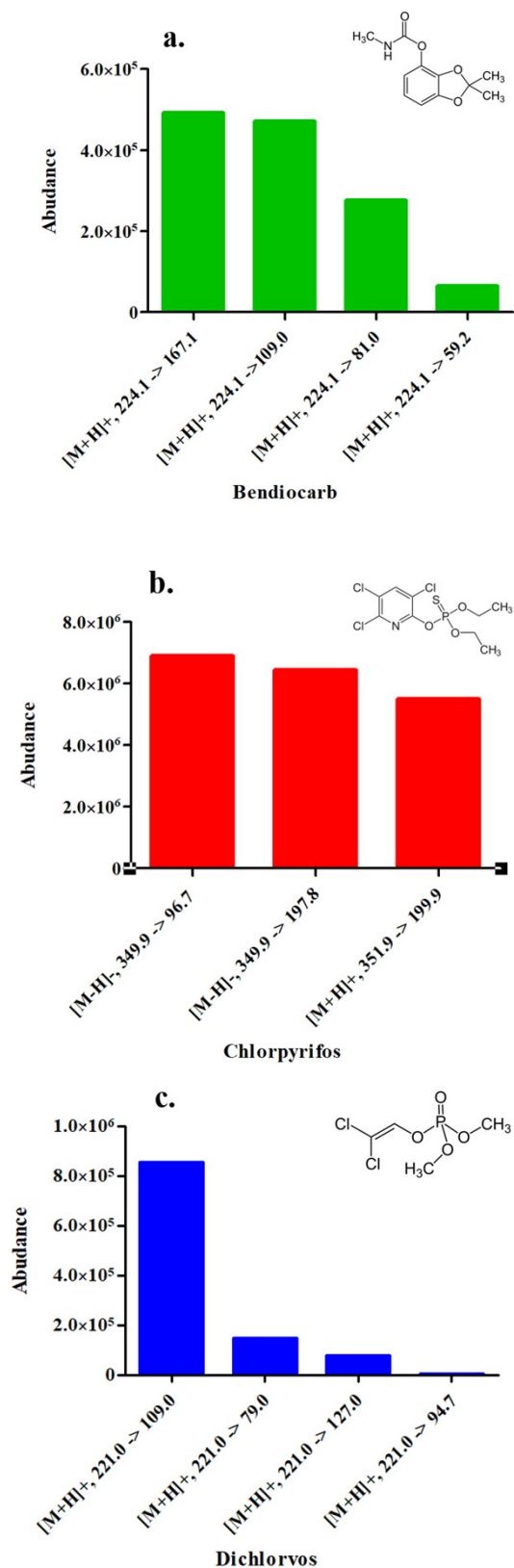


Figure S1. Selection of the most abundant transitions for a. bendiocarb, b. chlorpyrifos and c. dichlorvos. The same process was followed to obtain the optimum conditions for all the analytes (see Table S2).

2. Targeted pesticide residue list

Table S2. Analyte dependent parameters of the UHPLC-QqQ-MS method in the ESI+ mode.

No	Analyte	logP	Retention time [min]	Precursor ion [<i>m/z</i>]	Product ions [<i>m/z</i>]	CE (V)
1	Acephate	-0.85	2.44	184.1 [M+H] ⁺	143.0/49.0	8/16
2	Aldicarb	1.1	4.07	208.0 [M+NH ₄] ⁺	116.0/89.1	4/16
3	Aldicarb-sulfone	-0.6	2.66	240.1 [M+NH ₄] ⁺	148.1/86.1	12/24
4	Aldicarb-sulfoxide	-0.2	2.57	207.1 [M+H] ⁺	132.0/89.1	4/13
5	Azinphos-ethyl	3.4	8.05	346.1 [M+H] ⁺	132.1/77.0	18/44
6	Azinphos-methyl	2.8	6.52	318.08 [M+H] ⁺	132.1/77.0	44/64
7	Bendiocarb	1.7	4.67	224.1 [M+H] ⁺	167.1/109.0	8/20
8	Cadusafos	3.3	9.84	271.0 [M+H] ⁺	215.0/159.0	8/12
9	Carbaryl	2.4	5.02	202.0 [M+H] ⁺	144.9/127.1	8/34
10	Carbofuran	2.3	4.75	222.1 [M+H] ⁺	165.1/123.1	10/22
11	Carbofuran-3-hydroxy	1.2	3.32	255.1 [M+NH ₄] ⁺	220.0/163.1	8/20
12	Carbophenothion	5.3	11.26	345.0 [M+H]/343.0 [M+H]	159.0/57.0	12/12
13	Chlorbufam	3.1	7.85	241.0 [M+NH ₄] ⁺ /226.0 [M+H]	154.0/174.0	40/16
14	Chlorfenvinphos	3.1	9.15	361.0 [M+H] ⁺ /359.0 [M+H] ⁻	155.1/155.1	10/8
15	Chlorpropham	3.5	5.95	214.0 [M+H]	172.0/154.0	16/24
16	Chlorpyrifos	5.3	10.97	349.9 [M+H] ⁻	198.8/96.7	24/40
17	Chlorpyrifos-methyl	4.3	9.70	323.9 [M+H] ⁺ /321.9 [M+H] ⁻	125/125	22/20
18	Demeton-S-methyl	1	4.88	231.0 [M+H] ⁺	89.1/61.0	12/36
19	Demeton-S-methyl-sulfone	-0.3	2.81	263.1 [M+H] ⁺	169.1/109	16/36
20	Desmedipham	3.4	6.25	300.9 [M+H] ⁺	181.8/135.7	4/20
21	Diazinon	3.8	9.20	305.1 [M+H] ⁺	169.1/96.9	22/44
22	Dichlorvos	1.4	4.59	221.0 [M+H]	109.0/79.0	20/20
23	Dicrotophos	0	2.98	238.1 [M+H] ⁺	112.1/72.1	10/26
24	Diethofencarb	2.8	6.91	268.1 [M+H] ⁺	226.1/124.0	8/36
25	Dimethoate	0.8	3.41	230.1 [M+H] ⁺	199.0/125.1	8/20
26	Disulfoton	4	9.66	275.0 [M+H] ⁺	89.0/61.0	5/40
27	Disulfoton-sulfone	1.9	5.66	307.0 [M+H] ⁺	124.9/96.9	16/32
28	Disulfoton-sulfoxide	1.7	5.51	291.1 [M+H] ⁺	213.0/185.2	8/12
29	EPN	4.4	9.79	324.0 [M+NH ₄] ⁺	296.1/157	12/26
30	Ethiofencarb	1.9	5.34	226.1 [M+H] ⁺	163.9/107.0	4/20
31	Ethion	5.1	10.86	385.0 [M+H] ⁺	199.0/143.0	8/24
32	Fenamiphos	3.2	8.49	304.1 [M+H] ⁺	217.0/202.0	24/44
33	Fenamiphos-sulfone	2	4.88	336.1 [M+H] ⁺	308.1/266.0	16/16
34	Fenamiphos-sulfoxide	1.8	4.71	320.1 [M+H] ⁺	233.1/108.1	28/44
35	Fenobucarb	2.8	6.58	208.1 [M+H] ⁺	77.1/95.0	44/16
36	Fenoxycarb	4.3	8.37	302.1 [M+H] ⁺	116.1/88.1	8/16
37	Fensulfothion	2.2	5.85	309.1 [M+H] ⁺	281.0/253.0	12/16
38	Fensulfothion-oxon	1.4	3.75	293.1 [M+H] ⁺	265.1/237.0	12/20
39	Fensulfothion-PO-sulfone	1.5	3.92	309.0 [M+H] ⁺	253.0/175.0	16/32
40	Fensulfothion-sulfone	2.6	6.08	325.0 [M+H] ⁺	269.0/191.0	12/24
41	Fenthion	4.1	8.91	279.1 [M+H] ⁺	247.0/169.0	12/18
42	Fenthion-sulfone	2.8	5.12	311.1 [M+H] ⁺	137.1/125.0	16/24
43	Fenthion-sulfoxide	2.7	4.87	295.0 [M+H] ⁺	280.1/109.1	20/36

44	Fonofos	3.9	8.98	247.1 [M+H] ⁺	137.0/109.0	8/22
45	Formetanate	1.2	2.46	222.0 [M+H] ⁺	165.1/120.0	12/32
46	Formothion	1.5	4.19	258.0 [M+H] ⁺	199.0/170.9	4/12
47	Fosthiazate	2.0	5.44	284.2 [M+H] ⁺	228.0/104.0	8/24
48	Furathiocarb	4.7	10.55	383.2 [M+H] ⁺	195.0/167.0	16/24
49	Heptenophos	1.3	6.10	251.0 [M+H] ⁺	127.0/124.9	24/20
50	Iprovalicarb	3.7	8.03	321.2 [M+H] ⁺	203.1/119.1	4/20
51	Isofenfos-methyl	3.3	8.90	332.1 [M+H] ⁺	273.0/230.9	4/12
52	Isofenphos	4.1	9.50	346.1 [M+H] ⁺	244.9/216.9	10/24
53	Isoprocarb	2.3	5.73	194.2 [M+H] ⁺	137.1/95.0	6/14
54	Malaoxon	0.6	4.79	315.0 [M+H] ⁺	126.9/99.0	12/28
55	Malathion	2.4	7.55	331.0 [M+H] ⁺	284.9/126.8	4/8
56	Mecarbam	2.4	8.05	330.0 [M+H] ⁺	227.0/97.1	4/48
57	Methacrifos	1.9	6.60	241.0 [M+H] ⁺	209.1/125.0	6/20
58	Methamidophos	-0.9	2.10	141.9 [M+H] ⁺	125.0/94.1	12/16
59	Methidathion	2.4	6.36	302.9 [M+H] ⁺	145.0/85.0	4/24
60	Methiocarb	2.9	6.96	226.1 [M+H] ⁺	169.0/120.9	8/18
61	Methiocarb-sulfone	1.6	3.38	275.1 [M+NH ₄] ⁺	122.0/107.0	24/52
62	Methiocarb-sulfoxide	1.5	3.17	242.0 [M+H] ⁺	185.1/122.1	12/32
63	Methomyl	0.6	2.81	162.9 [M+H] ⁺	106.1/88.1	8/6
64	Metolcarb	1.7	4.32	166.1 [M+H] ⁺	108.9/93.9	8/36
65	Mevinphos (sum of isomers)	1.2	2.89	225.0 [M+H] ⁺	193.1/127.0	4/16
66	Molinate	3.2	7.48	188.1 [M+H] ⁺	55.1/126.1	28/12
67	Monocrotophos	-0.2	2.89	224.1 [M+H] ⁺	193.0/127.0	4/16
68	Omethoate	-0.9	2.53	214.1 [M+H] ⁺	183.0/125.0	8/24
69	Oxamyl	-0.5	2.66	237.0 [M+NH ₄] ⁺	90.1/72.1	4/10
70	Phenmedipham	3.6	6.41	318.1 [M+NH ₄] ⁺	168.1/136.0	12/28
71	Phenthoate	3.7	8.7	321.0 [M+H] ⁺	247.0/135.0	8/24
72	Phorate	3.6	9.34	261.0 [M+H] ⁺	199.0/75.1	4/8
73	Phorate-sulfone	2.0	5.71	310.0 [M+NH ₄] ⁺	171.0/96.9	12/40
74	Phorate-sulfoxide	1.8	5.55	277.0 [M+H] ⁺	142.8/96.9	20/44
75	Phosalone	4.4	9.42	385.0 [M+NH ₄] ⁺	182.0/110.9	18/40
76	Phosmet	2.8	6.58	317.9 [M+H] ⁺	160.0/133.0	20/44
77	Phosphamidon	1.3	4.31	300.1 [M+H] ⁺	226.8/174.1	12/8
78	Phoxim	4.4	9.28	299.1 [M+H] ⁺	129.1/77.1	10/36
79	Pirimicarb	1.7	4.52	239.1 [M+H] ⁺	182.2/72.1	12/24
80	Pirimicarb-desmethyl	1.6	3.26	225.1 [M+H] ⁺	168.1/72.1	16/28
81	Pirimiphos-ethyl	4.8	10.73	334.1 [M+H] ⁺	198.0/182.1	20/24
82	Pirimiphos-methyl	4.2	9.45	306.0 [M+H] ⁺	164.2/108.1	24/32
83	Profenofos	4.7	10.25	374.9 [M+H] ⁺	304.9/302.9	16/20
84	Propamocarb	1.2	2.58	189.1 [M+H] ⁺	102.0/74.2	20/32
85	Propham	2.6	5.72	180.1 [M+H] ⁺	138.1/120.1	4/18
86	Propoxur	1.5	4.69	210.1 [M+H] ⁺	168.1/111.1	4/16
87	Prosulfocarb	3.9	10.16	252.1 [M+H] ⁺	128.2/91.1	12/44
88	Prothiofos	4.9	12.0	344.9 [M+H] ⁺	240.9/133.0	12/56
89	Quinalphos	4.4	8.8	299.0 [M+H] ⁺	163.0/147.0	24/20
90	Sulfotep	3.9	8.89	323.0 [M+H] ⁺	115.0/96.9	32/56
91	Temephos	6.0	10.61	467.0 [M+H] ⁺	419.0/405.0/125.0	24/20/44
92	Terbufos	4.5	10.49	289.0 [M+H] ⁺	103.0/57.0	6/26
93	Terbufos-sulfone	2.5	6.86	321.1 [M+H] ⁺	171.0/96.9	8/44
94	Terbufos-sulfoxide	2.2	6.86	305.1 [M+H] ⁺	187.0/96.9	8/52
95	Thiodicarb	1.7	5.3	355.0 [M+H] ⁺	108.1/88.1	16/16
96	Thiometon	2.7	5.71	247.0 [M+H] ⁺	89.1/61.0	6/40
97	Vamidothion	0.3	3.29	288.1 [M+H] ⁺	146.0/118.0	12/32

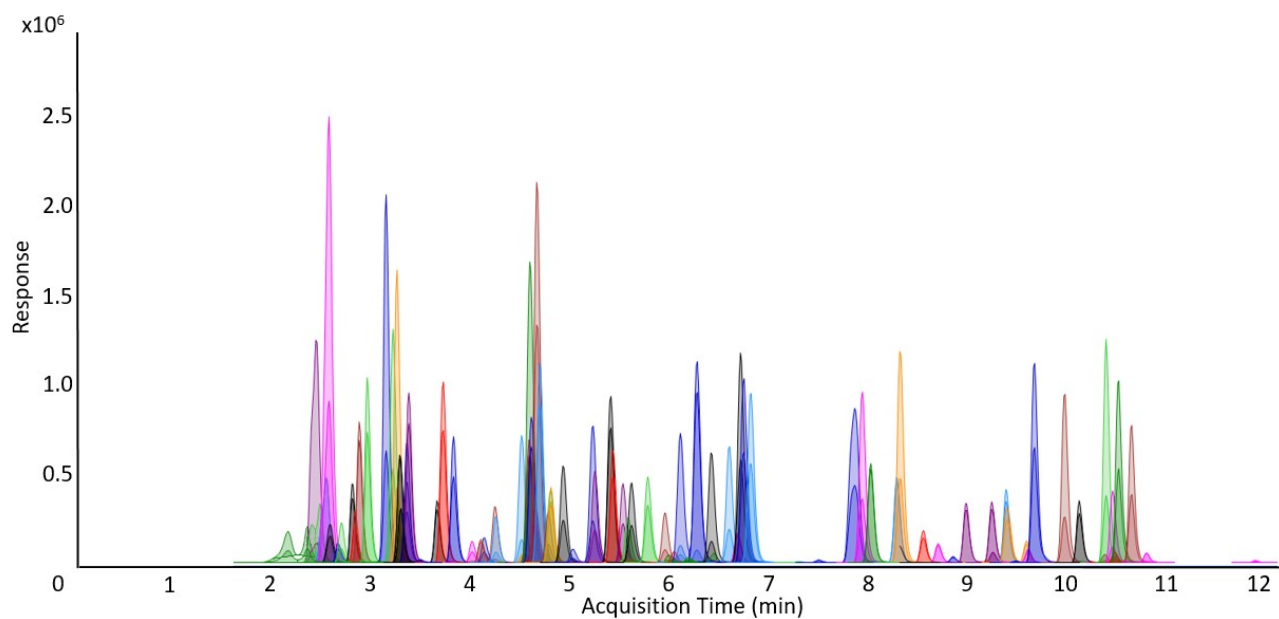


Figure S2. Extracted ion chromatogram (XIC) for the 97 analytes analyzed in matrix-matched standard at 0.040 mg kg^{-1} .

3. UHPLC-q-Orbitrap MS validation data in wheat flour matrix

Table S3. The validation data of the UHPLC-QqQ-MS method in wheat flour matrix. In detail, recovery (R%) rates, repeatability in terms of relative standard deviation% (RSD%) (0.004 mg Kg⁻¹ and 0.040 mg Kg⁻¹, n = 6), limits of quantification (LOQ) and matrix effect (ME%).

No	Analyte	Chemical group	Linear part (r ² >0.99)	R% at 0.004 mg Kg ⁻¹	RSD% at 0.004 mg Kg ⁻¹	R% at 0.040 mg Kg ⁻¹	RSD% at 0.040 mg Kg ⁻¹	LOQ (mg Kg ⁻¹)	ME% at 0.040 mg Kg ⁻¹
1	Acephate	OP	0.002-0.200	75	1	75	2	0.002	26
2	Aldicarb	CM	0.004-0.200	87	3	89	3	0.004	11
3	Aldicarb-sulfone	CM	0.002-0.200	80	0	78	4	0.002	25
4	Aldicarb-sulfoxide	CM	0.002-0.200	83	3	80	4	0.002	37
5	Azinphos-ethyl	OP	0.002-0.200	91	5	91	2	0.002	-1
6	Azinphos-methyl	OP	0.002-0.200	88	5	90	3	0.002	1
7	Bendiocarb	CM	0.002-0.200	88	5	90	1	0.002	5
8	Cadusafos	OP	0.002-0.200	88	3	90	2	0.002	6
9	Carbaryl	CM	0.002-0.200	88	3	87	1	0.002	11
10	Carbofuran	CM	0.002-0.200	87	3	89	1	0.002	6
11	Carbofuran-3-hydroxy	CM	0.002-0.200	82	3	83	4	0.002	17
12	Carbophenothion	OP	0.004-0.200	81	3	78	2	0.004	13
13	Chlorbufam	CM	0.040-0.400	<LOQ	-	97	4	0.040	73
14	Chlorfenvinphos	OP	0.002-0.200	93	5	91	2	0.002	-9
15	Chlorpropham	CM	0.02-0.400	<LOQ	-	93	6	0.020	-1
16	Chlorpyrifos	OP	0.004-0.200	90	5	85	2	0.004	6
17	Chlorpyrifos-methyl	OP	0.010-0.200	<LOQ	-	90	2	0.010	9
18	Demeton-S-methyl	OP	0.002-0.200	78	4	80	3	0.002	12
19	Demeton-S-methyl-sulfone	OP	0.002-0.200	84	4	82	3	0.002	31
20	Desmedipham	CM	0.002-0.200	88	3	89	2	0.002	5
21	Diazinon	OP	0.002-0.200	87	5	89	1	0.002	8
22	Dichlorvos	OP	0.004-0.200	116	14	113	3	0.004	5
23	Dicrotophos	OP	0.002-0.200	85	0	84	2	0.002	23
24	Diethofencarb	CM	0.002-0.200	89	2	92	2	0.002	-1

25	Dimethoate	OP	0.002-0.200	83	3	84	1	0.002	18
26	Disulfoton	OP	0.004-0.200	94	9	83	5	0.004	19
27	Disulfoton-sulfone	OP	0.002-0.200	91	2	91	1	0.002	-9
28	Disulfoton-sulfoxide	OP	0.002-0.200	92	3	92	1	0.002	5
29	EPN	OP	0.010-0.200	<LOQ	-	95	3	0.010	-8
30	Ethiofencarb	CM	0.002-0.200	76	5	80	3	0.002	9
31	Ethion	OP	0.002-0.200	85	4	86	2	0.002	10
32	Fenamiphos	OP	0.002-0.200	88	5	88	2	0.002	1
33	Fenamiphos-sulfone	OP	0.002-0.200	89	4	90	0	0.002	-11
34	Fenamiphos-sulfoxid	OP	0.002-0.200	92	3	91	1	0.002	-6
35	Fenobucarb	CM	0.010-0.200	<LOQ	-	92	2	0.010	6
36	Fenoxycarb	CM	0.002-0.200	86	6	86	1	0.002	2
37	Fensulfothion	OP	0.002-0.200	92	4	92	4	0.002	-5
38	Fensulfothion-oxon	OP	0.002-0.200	86	2	86	3	0.002	-2
39	Fensulfothion-PO-sulfon	OP	0.002-0.200	86	2	87	2	0.002	-13
40	Fensulfothion-sulfone	OP	0.002-0.200	93	3	91	1	0.002	-23
41	Fenthion	OP	0.004-0.200	90	4	90	2	0.004	1
42	Fenthion-sulfone	OP	0.002-0.200	95	5	91	1	0.002	-22
43	Fenthion-sulfoxide	OP	0.002-0.200	88	3	90	1	0.002	-5
44	Fonofos	OP	0.010-0.200	<LOQ	-	91	4	0.010	12
45	Formetanate	CM	0.002-0.200	83	3	83	1	0.002	13
46	Formothion	OP	0.004-0.200	84	2	83	2	0.004	-7
47	Fosthiazate	OP	0.002-0.200	91	2	90	2	0.002	6
48	Furathiocarb	CM	0.002-0.200	90	4	92	1	0.002	3
49	Heptenophos	OP	0.002-0.200	90	0	91	2	0.002	8
50	Iprovalicarb	CM	0.002-0.200	91	4	91	2	0.002	3
51	Isofenfos-methyl	OP	0.002-0.200	88	5	92	4	0.002	10
52	Isofenphos	OP	0.002-0.200	93	6	94	3	0.002	12
53	Isoproc carb	CM	0.004-0.200	92	3	89	2	0.004	2
54	Malaoxon	OP	0.002-0.200	88	3	89	3	0.002	10
55	Malathion	OP	0.002-0.200	92	3	90	2	0.002	-1
56	Mecarbam	OP	0.002-0.200	92	3	91	2	0.002	9

57	Methacrifos	OP	0.010-0.200	<LOQ	-	92	2	0.010	37
58	Methamidophos	OP	0.002-0.200	70	0	70	1	0.002	11
59	Methidathion	OP	0.002-0.200	88	3	89	3	0.002	6
60	Methiocarb	CM	0.002-0.200	91	2	90	3	0.002	5
61	Methiocarb-sulfone	CM	0.002-0.200	85	4	85	1	0.002	9
62	Methiocarb-sulfoxide	CM	0.002-0.200	82	3	82	2	0.002	19
63	Methomyl	CM	0.004-0.200	86	2	84	2	0.004	35
64	Metolcarb	CM	0.002-0.200	88	3	87	3	0.002	6
65	Mevinphos (sum of isomers)	OP	0.004-0.200	89	2	85	1	0.004	11
66	Molinate	CM	0.010-0.200	<LOQ	-	91	1	0.010	4
67	Monocrotophos	OP	0.002-0.200	82	3	82	1	0.002	30
68	Omethoate	OP	0.002-0.200	78	4	78	2	0.002	26
69	Oxamyl	CM	0.002-0.200	81	3	79	3	0.002	65
70	Phenmedipham	CM	0.002-0.200	89	4	89	2	0.002	2
71	Phenthoate	OP	0.002-0.200	90	4	91	1	0.002	1
72	Phorate	OP	0.004-0.200	88	6	91	4	0.004	11
73	Phorate-sulfone	OP	0.002-0.200	87	3	89	2	0.002	2
74	Phorate-sulfoxide	OP	0.002-0.200	90	0	89	2	0.002	6
75	Phosalone	OP	0.002-0.200	89	2	91	3	0.002	2
76	Phosmet	OP	0.002-0.200	90	0	92	1	0.002	-7
77	Phosphamidon	OP	0.002-0.200	89	2	90	1	0.002	-80
78	Phoxim	OP	0.002-0.200	90	4	89	1	0.002	-7
79	Pirimicarb	CM	0.002-0.200	88	3	89	1	0.002	4
80	Pirimicarb-desmethyl	CM	0.002-0.200	84	2	82	3	0.002	20
81	Pirimiphos-ethyl	OP	0.002-0.200	88	3	87	4	0.002	13
82	Pirimiphos-methyl	OP	0.002-0.200	90	4	90	2	0.002	5
83	Profenophos	OP	0.002-0.200	90	5	90	1	0.002	-2
84	Propamocarb	CM	0.002-0.200	83	3	79	2	0.002	22
85	Propham	CM	0.004-0.200	91	5	91	3	0.004	3
86	Propoxur	CM	0.002-0.200	89	2	90	1	0.002	10
87	Prosulfocarb	CM	0.002-0.200	88	5	89	2	0.002	-1
88	Prothiofos	OP	0.020-0.400	<LOQ	-	74	5	0.020	43

89	Quinalphos	OP	0.002-0.200	92	4	90	2	0.002	-1
90	Sulfotep	OP	0.002-0.200	90	4	90	1	0.002	4
91	Temephos	OP	0.002-0.200	89	7	86	2	0.002	-19
92	Terbufos	OP	0.002-0.200	91	5	89	3	0.002	5
93	Terbufos-sulfone	OP	0.002-0.200	89	2	88	3	0.002	3
94	Terbufos-sulfoxide	OP	0.002-0.200	89	4	90	2	0.002	8
95	Thiodicarb	CM	0.004-0.200	85	5	84	1	0.004	3
96	Thiometon	OP	0.040-0.400	<LOQ	-	82	3	0.04	7
97	Vamidotion	OP	0.002-0.200	83	3	84	2	0.002	18

*OP= organophosphate & CM= carbamate