

Supporting information

Quantification of pesticide residues on plastic mulching films in typical farmlands of the North China

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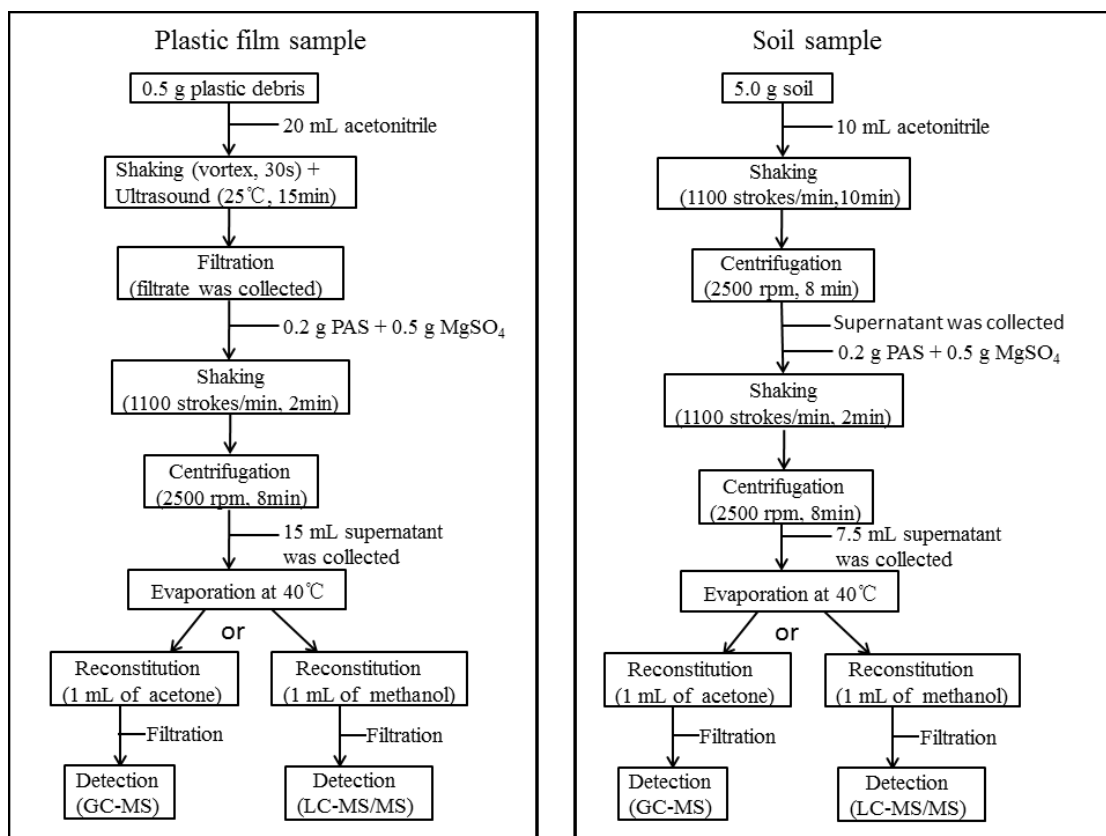


Figure S1. Flow chart of sample preparation

Table S1 Parameters of pesticides detected by GC-MS

No.	Pesticides	Retention time (min)	Quantitative ion (m/z)	Qualitative ion (m/z)
1	Trifluralin	10.105	306.1	264.0
2	Procymidone	13.286	96.1	283.0
3	Oxyfluorfen	13.929	252.0	361.0
4	Chlorfenapyr	14.179	59.0	247.1
5	Bifenthrin	15.495	181.1	166.1
6	Fenpropathrin	15.592	97.1	125.0
7	Cyhalothrin	16.250	181.0	197.0

Table S2 Parameters of pesticides detected by LC-MS/MS

No.	Pesticides	Retention time (min)	Ionization mode	Quantitative ion pair (m/z)	Qualitative ion pair (m/z)	Collision energy (V)
1	Flonicamid	2.85	+	229.9/203.1	229.9/174.0	15, 14
2	Thiamethoxam	2.86	+	291.9/211.1	291.9/132.0	9, 16
3	Acetamiprid	3.09	+	223.0/126.1	223.0/90.2	18, 31
4	Thiacloprid	3.15	+	252.8/126.1	252.8/90.2	17, 32
5	Tricyclazole	3.25	+	189.9/163.1	189.9/136.1	21, 26
6	Imazalil	3.40	+	296.9/159.0	296.9/255.0	21, 17
7	Flumioxazin	3.63	+	354.9/299.1	354.9/327.1	27, 20
8	Atrazine	3.66	+	216.0/174.1	216.0/104.1	10, 22
9	Azoxystrobin	3.66	+	404.0/372.1	404.0/344.1	12, 22
10	Boscalid	3.81	+	343.0/307.1	343.0/271.1	18, 29
11	Dimethomorph	3.85	+	387.9/301.1	387.9/165.0	18, 28
12	Myclobutanil	3.88	+	289.0/70.3	289.0/125.1	18, 28
13	Triadimefon	3.90	+	293.9/197.1	293.9/69.3	13, 18
14	Cyazofamid	3.98	+	324.9/108.1	324.9/217.1	11, 17
15	Thifluzamide	3.99	+	528.6/489.0	528.6/509	28, 16

16	Flusilazole	4.06	+	315.9/247.1	315.9/165.1	25, 18
17	Tebufenozide	4.06	+	353.0/133.1	353.0/105.2	16, 31
18	Acetochlor	4.08	+	270.0/224.1	270.0/133.1	9, 28
19	Tebuconazole	4.20	+	308.0/70.2	308.0/125.1	22, 31
20	Indoxacarb	4.31	+	527.9/203.0	527.9/150.0	39, 20
21	Hexaconazole	4.34	+	313.9/70.2	313.9/159.0	17, 26
22	Hexaflumuron	4.36	-	458.7/438.9	458.7/275.8	14, 21
23	Difenoconazole	4.40	+	405.9/251.0	405.9/188.0	23, 41
24	Lufenuron	4.66	+	510.8/158.0	510.8/141.0	30, 17
25	Machette	4.83	+	312.0/238.1	312.0/162.2	9, 19
26	Etoxazole	5.06	+	360.0/141.0	360.0/304.1	28, 15
27	Butralin	5.21	+	296.0/240.1	296.0/222.1	10, 20
28	Pyridaben	5.54	+	364.9/147.1	364.9/309.1	22, 9

Table S3. Results of method validation

No.	Pesticides	Calibration Curves	R ²	Linear range (ng/g)	LOD (ng/g)	LOQ (ng/g)
1	Flonicamid	Y = -11178+4397.46*X	0.9999	5-200	1.00	5.00
2	Thiamethoxam	Y = 84922+11942.5*X	0.9990	5-200	0.10	0.50
3	Acetamiprid	Y = 66715.5+16021.7*X	0.9996	5-200	0.10	0.50
4	Thiacloprid	Y = 127872+21661*X	0.9991	5-200	0.19	0.50
5	Tricyclazole	Y = 351944+46687.6*X	0.9992	5-200	0.05	0.10
6	Imazalil	Y = 157978+23057.3*X	0.9990	5-200	0.01	0.30
7	Flumioxazin	Y = -2660.17+628.207*X	0.9990	5-200	0.30	5.00
8	Atrazine	Y = -9322.96+23330.8*X	0.9999	5-200	0.01	0.05
9	Azoxystrobin	Y = -384142+93351*X	0.9997	5-200	0.01	0.23
10	Boscalid	Y = 204195+15375.4*X	0.9972	5-200	0.01	0.50
11	Dimethomorph	Y = -150326+43337.3*X	0.9995	5-200	0.05	0.18
12	Myclobutanil	Y = 84301.8+16229*X	0.9991	5-200	0.05	0.10

13	Triadimefon	$Y = 32473.1 + 29324.3 * X$	0.9996	5-200	0.02	0.05
14	Cyazofamid	$Y = 9911.07 + 4023.63 * X$	0.9995	5-200	0.04	1.00
15	Thifluzamide	$Y = 35818.7 + 3951.55 * X$	0.9961	5-200	0.10	0.50
16	Flusilazole	$Y = -49785.8 + 81656.4 * X$	0.9999	5-200	0.05	0.10
17	Tebufenozide	$Y = 111749 + 32188.4 * X$	0.9994	5-200	0.05	0.20
18	Acetochlor	$Y = 1753.75 + 2782.23 * X$	0.9997	5-200	1.00	5.00
19	Tebuconazole	$Y = -31939.5 + 21459.2 * X$	0.9999	5-200	0.20	0.50
20	Indoxacarb	$Y = 44831 + 6848.33 * X$	0.9986	5-200	0.05	0.50
21	Hexaconazole	$Y = 3382.49 + 16682.5 * X$	0.9999	5-200	0.10	0.50
22	Hexaflumuron	$Y = 121409 + 5414.76 * X$	0.9974	5-200	0.30	1.00
23	Difenoconazole	$Y = -125273 + 48694.9 * X$	0.9999	5-200	0.20	0.50
24	Lufenuron	$Y = -1135.98 + 856.009 * X$	0.9989	5-200	0.30	1.00
25	Machette	$Y = -20595.8 + 5351.7 * X$	0.9998	5-200	0.10	0.50
26	Etoxazole	$Y = 529548 + 161887 * X$	1.0000	5-200	0.01	0.05
27	Butralin	$Y = -26830.8 + 23122.7 * X$	0.9999	5-200	0.01	0.05
28	Pyridaben	$Y = -61084.4 + 50587.7 * X$	0.9998	5-200	0.03	0.10
29	Trifluralin	$Y = -207.42 + 300.08 * X$	0.9992	10-200	2.00	5.00
30	Procymidone	$Y = -735.64 + 649.33 * X$	0.9996	10-200	1.00	2.50
31	Oxyfluorfen	$Y = -445.25 + 183.3 * X$	0.9994	10-200	2.00	5.00
32	Chlorfenapyr	$Y = -2528.4 + 889.8 * X$	0.9991	10-200	0.50	2.00
33	Bifenthrin	$Y = -2620.5 + 1678.8 * X$	0.9997	10-200	0.50	2.00
34	Fenpropathrin	$Y = -3032.4 + 518.31 * X$	0.9959	10-200	2.00	5.00
35	Cyhalothrin	$Y = -1173.4 + 331.56 * X$	0.9985	10-200	2.00	5.00

Table S4 Pesticides residues in soil samples (ng/g)

	Compounds	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	Freq	max	min
1	Flonicamid	1.0	ND	ND	ND	ND	ND	ND	ND	1.0	ND	ND	ND	ND	ND	ND	0.9	1.0	ND	ND	ND	20%	1.0	0.9
2	Thiamethoxam	ND	ND	ND	9.8	ND	2.9	ND	0.7	7.5	1.0	ND	ND	ND	ND	ND	ND	2.8	ND	ND	ND	30%	9.8	0.7
3	Acetamiprid	ND	0.5	ND	ND	ND	ND	ND	17.2	9.0	ND	ND	ND	0.4	0.5	0.6	0.5	36.9	0.3	5.2	0.5	55%	36.9	0.3
4	Thiacloprid	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
5	Tricyclazole	ND	ND	ND	1.2	0.8	ND	ND	ND	ND	0.9	ND	ND	ND	ND	ND	0.5	ND	ND	ND	ND	20%	1.2	0.5
6	Imazalil	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
7	Atrazine	3.8	1.3	2.5	0.8	1.7	2.1	1.1	81.5	28.8	1.4	4.2	7.5	4.0	2.1	3.1	2.2	1.2	0.9	4.7	3.4	100%	81.5	0.8
8	Flumioxazin	4.3	1.3	3.1	2.3	2.1	1.5	1.7	2.3	1.8	1.8	1.4	1.9	2.2	1.9	2.5	2.9	2.6	2.0	1.9	1.8	100%	4.3	1.3
9	Azoxystrobin	ND	ND	0.5	4.2	0.3	ND	0.7	ND	ND	0.4	ND	ND	ND	ND	ND	0.7	ND	ND	0.5	ND	35%	4.2	0.3
10	Boscalid	ND	ND	ND	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.0	9.7	ND	ND	ND	ND	15%	9.7	1.0
11	Dimethomorph	ND	ND	ND	ND	ND	ND	ND	1.9	51.6	ND	ND	ND	ND	0.4	6.7	5.7	0.3	ND	0.6	ND	35%	51.6	0.3
12	Myclobutanil	ND	ND	ND	ND	ND	0.9	ND	ND	0.7	0.8	ND	3.9	ND	ND	0.6	ND	ND	ND	ND	ND	25%	3.9	0.6
13	Triadimefon	0.7	0.4	5.8	0.7	0.7	0.5	0.6	17.6	62.2	0.9	1.0	0.6	0.5	2.1	0.8	0.9	0.7	ND	0.7	0.4	95%	62.2	0.4
14	Cyazofamid	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
15	Thifluzamide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
16	Flusilazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
17	Acetochlor	7.3	2.8	7.4	ND	1.4	1.4	ND	7.1	14.0	1.3	6.1	9.6	ND	ND	3.0	3.6	ND	ND	3.3	ND	65%	14.0	1.3
18	Tebufozide	ND	ND	ND	ND	ND	ND	ND	0.7	1.9	ND	ND	ND	4.2	ND	ND	ND	ND	ND	ND	ND	15%	4.2	0.7
19	Tebuconazole	ND	ND	ND	ND	ND	2.7	ND	ND	ND	ND	ND	ND	ND	ND	1.1	1.3	ND	ND	ND	ND	15%	2.7	1.1
20	Indoxacarb	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
21	Hexaconazole	ND	ND	ND	0.5	0.5	0.8	ND	ND	2.9	ND	ND	ND	ND	ND	0.8	ND	ND	ND	ND	ND	25%	2.9	0.5
22	Hexaflumuron	ND	ND	ND	3.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5%	3.4	3.4
23	Difenoconazole	ND	ND	4.3	ND	ND	ND	ND	ND	1.0	ND	ND	ND	0.6	0.6	2.3	25.3	ND	ND	1.6	ND	35%	25.3	0.6
24	Lufenuron	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.5	5.9	ND	0.8	ND	ND	15%	5.9	0.5

25	Machette	ND	ND	4.7	128.6	2.3	21.5	ND	40.5	54.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30%	128.6	2.3
26	Etoazole	ND	ND	ND	ND	ND	1.2	ND	ND	ND	ND	ND	ND	ND	1.3	ND	ND	ND	1.5	ND	ND	ND	15%	1.5	1.2
27	Butralin	408.6	1.1	9.1	ND	21.0	26.5	ND	ND	21.5	ND	468.4	ND	1.9	1.9	2.6	ND	0.7	0.6	1.7	1.7	70%	468.4	0.6	
28	Pyridaben	ND	0.9	ND	1.2	ND	ND	ND	8.9	52.1	1.8	ND	ND	ND	ND	9.7	3.1	19.6	1.4	77.4	ND	50%	77.4	0.9	
29	Trifluralin	ND	ND	ND	ND	160.9	1.8	ND	1.1	ND	1.5	ND	1.2	ND	ND	1.1	ND	ND	ND	ND	ND	30%	160.9	1.1	
30	Procymidone	ND	ND	ND	6.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.9	18.8	6.5	ND	ND	ND	20%	18.8	6.1	
31	Oxyfluorfen	ND	ND	ND	ND	ND	ND	ND	ND	18.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	8.0	ND	10%	18.1	8.0	
32	Chlorfenapyr	ND	8.0	3.4	2.0	ND	8.2	5.1	6.2	33.5	ND	ND	ND	397.1	23.7	4.7	15.9	96.7	2.6	2.7	44.3	75%	397.1	2.0	
33	Bifenthrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	34.2	ND	5%	34.2	34.2	
34	Fenpropathrin	ND	ND	ND	ND	ND	ND	ND	ND	21.6	ND	ND	ND	ND	ND	ND	ND	189.0	ND	ND	ND	10%	189.0	21.6	
35	Cyhalothrin	ND	ND	ND	ND	ND	ND	ND	16.3	7.9	6.9	3.7	3.9	124.3	26.0	5.3	ND	ND	ND	ND	6.2	45%	124.3	3.7	
	total concentration	425.7	16.3	40.8	163.1	191.6	72.1	9.3	202.0	391.5	18.6	484.8	28.6	535.3	60.5	55.5	97.7	357.9	10.1	142.5	58.3				
	amount of pesticides	6	8	9	13	10	13	5	13	19	11	6	7	9	10	18	16	12	8	13	7				

Table S5 Pesticides residues in plastic film sample (ng/g)

No	Compounds	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	Freq	max	min
1	Flonicamid	ND	ND	11.5	ND	ND	ND	ND	ND	ND	7.2	ND	ND	ND	ND	ND	ND	ND	ND	20.3	ND	15%	20.3	7.2
2	Thiamethoxam	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9.9	ND	ND	ND	ND	ND	5%	9.9	9.9
3	Acetamiprid	85.1	9.1	5.6	16.5	8.8	ND	12.5	23.5	14324.	17.3	6.9	103.	13.1	7.2	7.2	61.9	214.7	753.9	52.0	7.2	95%	14324.	5.6
										8			2										8	
4	Thiacloprid	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
5	Tricyclazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
6	Imazalil	20.0	ND	ND	ND	ND	ND	36.0	ND	ND	25.3	31.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	20%	36.0	20.0
7	Atrazine	46.7	50.4	8.5	12.5	39.5	7.7	74.1	71.2	162.1	14.7	18.1	60.0	40.3	32.5	326.	86.1	44.5	80.8	110.4	166.	100	326.1	7.7
																1					9	%		
8	Flumioxazin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.3	ND	ND	ND	ND	ND	19.2	ND	10%	19.2	16.3
9	Azoxystrobin	ND	28.8	25.9	13.9	18.1	ND	ND	ND	14.7	42.9	ND	29.6	34.1	14.1	23.2	ND	29.1	12.0	19.2	12.3	70%	42.9	12.0
10	Boscalid	7.7	ND	5.3	ND	5.6	8.3	20.5	3.2	3.2	28.0	209.1	3.2	5.9	6.7	6.1	ND	6.9	4.5	31.2	3.7	85%	209.1	3.2
11	Dimethomorph	ND	ND	ND	10.9	ND	ND	11.5	239.	9.9	ND	ND	68.3	10.9	ND	ND	ND	9.1	ND	12.8	ND	40%	239.5	9.1
																							5	
12	Myclobutanil	3.2	3.5	5.6	3.7	4.3	ND	3.5	12.0	17.1	6.7	5.3	8.8	6.7	4.0	13.9	9.9	3.7	6.1	9.1	6.4	95%	17.1	3.2
13	Triadimefon	12.5	103.	6.9	21.1	69.9	24.	23.7	71.7	38.7	15.5	11.2	195.	38.1	39.5	77.6	176.8	25.6	19.2	27.2	56.0	100	195.7	6.9
			7																			%		
14	Cyazofamid	ND	ND	ND	ND	ND	ND	22.4	ND	ND	14.9	22.9	ND	ND	ND	ND	ND	16.5	ND	ND	ND	20%	22.9	14.9
15	Thifluzamide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
16	Flusilazole	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
17	Acetochlor	48.8	99.5	ND	29.3	54.1	15.	49.1	190.	43.5	78.9	69.9	49.3	167.2	102.	69.6	242.9	113.6	99.2	106.1	52.0	95%	242.9	15.2
																							2	4
18	Tebuconazole	9.6	9.9	ND	ND	ND	ND	15.2	ND	ND	9.6	10.1	ND	10.1	ND	7.5	ND	6.4	ND	7.7	ND	45%	15.2	6.4
19	Tebuconazole	5.9	6.4	4.5	8.3	55.5	5.6	6.7	8.8	7.5	109.	9.9	4.5	9.6	8.8	7.5	10.1	10.1	6.1	7.2	9.1	100	109.6	4.5

		6																				%		
20	Indoxacarb	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5%	7.5	7.5
21	Hexaconazole	19.2	ND	ND	ND	11.7	ND	26.9	2.9	6.7	26.7	44.8	3.5	6.1	4.5	ND	ND	9.3	ND	12.5	ND	60%	44.8	2.9
22	Hexaflumuron	5.6	5.1	ND	6.1	361.	6.9	ND	54.4	6.4	ND	ND	ND	6.7	ND	ND	ND	ND	ND	ND	ND	40%	361.9	5.1
		9																						
23	Difenoconazole	6.1	100.	6.9	13.6	ND	ND	7.2	6.1	9.1	10.1	6.7	4.8	12.5	62.7	8.5	8.3	9.6	5.9	29.9	6.4	90%	100.8	4.8
		8																						
24	Lufenuron	ND	ND	ND	12.8	ND	ND	ND	ND	ND	9.1	10.1	ND	ND	41.6	ND	ND	10.1	ND	16.0	ND	30%	41.6	9.1
25	Machette	16.8	23.2	16.5	26.1	23.5	18.	23.5	114.	13.9	27.7	30.1	54.9	ND	46.7	ND	35.2	23.2	ND	ND	ND	75%	114.9	13.9
		1 9																						
26	Etoazole	ND	ND	ND	2.4	ND	ND	5.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10%	5.1	2.4
27	Butralin	38.1	17.6	ND	ND	18.1	ND	ND	12.0	14.1	13.3	4.5	80.5	ND	ND	ND	20.3	ND	33.3	7.7	6.4	60%	80.5	4.5
28	Pyridaben	ND	ND	ND	ND	ND	ND	ND	103.	18.4	ND	ND	17.1	ND	ND	ND	ND	11.2	ND	21.6	ND	25%	103.5	11.2
		5																						
29	Trifluralin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0%	0.0	0.0
30	Procymidone	ND	ND	ND	ND	ND	ND	ND	ND	57.3	ND	ND	ND	51.3	58.9	28.5	ND	111.2	ND	74.1	ND	30%	111.2	28.5
31	Oxyfluorfen	ND	ND	ND	31.2	ND	ND	ND	ND	28.5	ND	26.9	ND	21.6	ND	ND	22.7	27.5	26.7	25.3	ND	40%	31.2	21.6
32	Chlorfenapyr	138.	90.4	54.1	347.	199.	ND	2323.	ND	90.4	136.	522.1	26.9	20677.	46.1	65.3	301.6	548.8	1413.	1023.7	149.	90%	20677.	26.9
		4 2 5 7 0 6 6 1 6																						
33	Bifenthrin	ND	ND	ND	117.	ND	ND	ND	ND	ND	25.6	392.3	ND	ND	ND	ND	91.7	ND	ND	10820.	ND	25%	10820.	25.6
		1 8 8																						
34	Fenpropathrin	ND	ND	ND	ND	ND	ND	341.3	ND	ND	144.	183.2	ND	ND	ND	ND	963.2	1133.	ND	ND	25%	1133.6	144.	
		0 6 0																						
35	Cyhalothrin	ND	ND	ND	ND	ND	ND	149.6	ND	ND	ND	1041.	ND	1085.1	ND	37.1	89.9	ND	ND	147.7	ND	30%	1085.1	37.1

										6										
total concentration	463.	548.	151.	672.	870.	86.	3152.	914.	14866.	770.	2657.	710.	22213.	476.	688.	1157.	2194.	3594.	12601.	475.
	7	3	5	8	4	4	5	1	1	7	6	4	2	3	0	3	4	9	9	5
amount of pesticides	15	13	11	16	13	7	18	14	18	21	20	15	18	14	14	13	20	13	22	11
