

## Supporting Information

### Simultaneous Extraction of Pesticides and Polycyclic Aromatic Hydrocarbons in Brazilian Cachaça using a Modified QuEChERS Method followed by GC-MS/MS Quantification

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**Table S1. Retention Time, Quantification and Confirmation Transitions and Collision Energies Optimized for Pesticides and PAHs**

analyte	retention time (min)	transition 1 (quantification) ( <i>m/z</i> )	CE1 <sup>a</sup>	transition 2 (confirmation) ( <i>m/z</i> )	CE2 <sup>a</sup>
PESTICIDES					
thiobencarb	6.03	100.0–55.0	25	100.0–72.0	5
dichlorvos	6.55	185.0–93.0	15	185.0–109.0	15
carbofuran	6.89	164.0–149.1	15	164.0–131.0	15
disulfoton sulfone	7.24	186.0–97.1	15	186.0–81.0	20
2,4-D	7.34	174.6–146.9	15	144.6–109.0	5
mervinphos	8.07	191.9–127.0	10	127.0–109.0	10
trifluralin	10.15	305.5–264.2	5	305.5–160.0	25
fenobucarb	10.19	150.0–121.0	10	121.0–77.0	18
ethoprophos	10.47	158.2–97.0	15	200.1–158.0	5
benfluralin	10.49	292.0–264.0	5	292.0–206.0	15
promecarb	11.38	149.9–135.1	15	149.9–91.0	25
disulfoton	11.66	88.1–60.0	5	88.1–59.0	25
dicloran	12.22	206.0–175.9	15	206.0–148.0	25
quintozene	12.46	236.5–117.0	25	236.5–119.1	25
heptachlor	12.47	235.0–141.0	25	235.0–117.0	35
dicamba	12.52	173.0–145.0	15	173.0–109.0	35
beta-HCH	12.58	180.5–145.2	15	218.5–183.1	15
simazine	12.73	173.0–138.1	5	173.0–110.1	15
gamma-HCH	13.04	180.5–145.2	15	218.5–183.1	15
etrimphos	13.09	181.0–153.0	6	292.0–181.0	16

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spiroxamine	13.36	144.0–100.0	15	198.0–126.0	5
iprobenfos	13.44	204.0–171.0	2	204.0–122.0	10
pirimicarb	13.79	238.0–166.0	20	166.0–96.0	15
dichlofluanide	13.79	167.0–124.0	5	167.0–97.0	25
vinclozolin	14.13	284.5–212.2	15	197.4–145.2	35
chlorpyrifos-methyl	14.22	288.0–93.0	25	288.0–273.0	15
alachlor	14.29	237.0–160.0	15	188.1–160.1	10
metribuzine	14.45	198.0–82.1	15	198.0–110.0	15
tolclofos-methyl	14.45	264.5–250.2	25	264.5–93.2	15
fenchlorphos	14.47	284.4–270.1	30	284.9–269.9	15
prometryn	14.67	241.2–183.9	10	241.0–199.0	10
ametryn	14.68	227.2–170.1	20	227.2–152.1	20
pirimiphos-methyl	14.86	290.1–125.0	25	290.1–233.0	10
chlorothalonil	14.90	266.0–231.0	25	265.2–231.0	25
aldrin	14.90	257.0–222.0	25	262.5–193.1	12
bentazone	14.98	198.0–92.0	25	119.0–92.0	10
fenitrothion	15.11	277.0–260.0	5	277.0–109.0	5
parathion-ethyl	15.51	291.1–109.0	10	291.1–81.0	40
tetraconazole	15.69	336.0–218.0	25	336.0–204.0	35
pirimiphos-ethyl	15.77	318.1 – 182.1	15	318.1 – 166.1	15
isodrin	15.77	262.8–193.0	35	192.9–123.0	35

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bromophos-methyl	15.82	330.9–315.9	20	331.0–93.0	10
chlorpyrifos	15.85	313.8–258.0	5	314.0–286.0	5
isocarbophos	15.88	289.0–136.0	5	289.0–113.0	5
isoxaflutole	16.07	279.0–252.0	15	279.0–189.0	15
cyprodinil	16.21	225.0–224.0	20	224.0–208.0	10
trans- chlordane	16.65	373.0–265.8	15	373.0–336.8	5
2,4-DDD	16.68	234.4–199.2	25	234.4–165.3	5
bromophos-ethyl	16.68	359.0–302.8	35	357.0–300.8	35
2,4-DDE	16.77	246.0–176.0	30	246.0–175.1	40
alpha-endosulfan	16.92	241.0–206.0	5	195.0–159.0	10
cis-chlordane	16.94	373.0–265.8	15	373.0–336.8	5
4,4-DDE	17.37	246.0–176.0	30	246.0–175.1	40
4,4-DDD	17.44	234.4–199.2	25	234.4–165.3	5
chlorfenson	17.50	174.5–111.2	15	174.5–75.2	15
oxyfluorfen	17.66	361.0–317.0	5	361.0–300.0	15
buprofezin	17.67	104.0–77.0	5	171.6–57.0	15
uniconazole-P	17.76	233.9–165.1	10	233.9–137.0	20
fluazifop-p-butyl	17.80	282.0–238.0	15	282.0–91.0	5
flusilazole	17.93	232.6–165.1	25	232.6–152.0	15
epoxiconazole	18.04	191.6–157.1	5	191.6–138.0	15
chlorfenapyr	18.05	247.0–227.0	15	408.0–59.0	10

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endrin	18.07	281.0–245.0	10	263.0–191.0	25
carboxin	18.10	235.0–143.0	5	235.0–162.1	10
chlorbenzylate	18.17	251.0–139.0	5	138.0–111.0	15
dicofol	18.17	251.0–139.0	15	253.0–141.0	14
ethion	18.47	231.0–129.0	8	231.0–175.0	25
carbofenotion	18.48	153.0–96.9	30	199.0–143.0	5
2,4-DDT	18.48	234.4–199.2	25	234.4–165.3	5
4,4-DDT	18.97	235.0–165.1	25	235.0 – 199.1	15
propiconazole	19.13	175.0–147.0	15	259.0–69.1	5
resmethrin	19.32	171.0–128.2	15	171.0–143.0	5
tebuconazole	19.41	250.2–125.1	15	250.2–153.1	5
acrinathrin	19.67	181.1–152.1	25	181.1–127.1	30
bifenthrin	19.67	181.0–165.0	25	181.0–139.0	25
hexazinone	19.71	171.3–71.1	15	171.3–85.1	15
iprodione	19.84	314.0–245.0	10	314.0–56.0	10
bromopropylate	19.88	183.0–155.0	15	341.0–183.0	15
epn	20.09	157.0–110.0	15	157.0–77.1	22
fenazaquin	20.17	160.0–117.0	25	160.0–145.2	20
mirex	20.63	271.6–236.8	35	236.6–118.9	25
triticonazole	20.66	216.5–182.1	5	234.4–182.1	10
fenoxaprop-ethyl	21.33	360.8–288.1	9	287.8–119.1	9

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azinphos-methyl	21.45	160.1–132.1	5	160.1–77.1	15
permethrin	21.64	163.0–127.0	10	183.1–168.1	15
coumaphos	22.03	362.0–109.0	15	362.0–81.0	35
cyfluthrin	22.25	163.0–127.0	10	165.0–91.0	15
cypermethrin	22.56	163.0–127.0	10	163.0–91.0	10
fenbuconazole	22.64	198.0–129.0	0	198.0–102.0	32
fenvalerate	24.30	167.0–125.0	5	225.0–119.0	15
deltamethrin	25.42	253.0–172.0	5	253.0–93.0	10
azoxystrobin	27.11	344.0–329.1	15	388.0–360.1	5
cinidon-ethyl	27.93	358.0–330.0	15	393.0–358.0	5
PAHs					
MCH	21.79	242.0 – 242.0	5	242.0 -239.1	40
BcFL	16.97	216.0 – 216.0	5	215.0 – 215.0	5
BaA	19.31	228.0 – 228.0	5	226.0 – 226.0	5
CHR	19.82	228.0 – 228.0	5	226.0 -224.0	25
CPP	20.25	226.0 – 226.0	5	228.0 – 228.0	5
BbFA	24.54	252.0 – 252.0	5	250.0 – 250.0	5
BkFA	24.63	252.0 – 252.0	5	252.0 – 250.0	25
BjFA	24.86	252.0 – 252.0	5	250.0 – 250.0	5
BaP	26.91	252.0 – 252.0	5	250.0 – 250.0	5
IP	30.51	274.0 – 274.0	5	276.0 – 276.0	5

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DBahA	32.81	278.0 – 278.0	5	276.0 – 276.0	5
BghiP	35.44	276.0 – 276.0	5	277.0 – 277.0	5
DBalP	47.83	302.0 – 302.0	5	303.0 – 303.0	5
DBaeP	52.48	302.0 – 302.0	5	303.0 – 303.0	5
DBaiP	55.69	302.0 – 302.0	5	300.0 – 300.0	5
DPahP	57.32	302.0 – 302.0	5	303.0 – 303.0	5

<sup>a</sup>CE: collision energy.

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**Table S2. Description about Procedures for Pesticides and PAHs Reported in the Literature**

matrix	number of analytes	extraction	analysis method	sample volume (mL)	solvents and total volumes (mL) spent
LITERATURE FOR PESTICIDES					
sorghum distilled spirit <sup>8</sup>	5	QuEChERS	GC-MS/MS <sup>a</sup>	5	acetonitrile: 10
distilled spirit of wine <sup>9</sup>	11	a- QuEChERS; b- sample pre-concentration; c- LLE <sup>b</sup>	a- GC-NPD <sup>c</sup> b- GC-ECD <sup>d</sup> c- HPLC-UV/vis <sup>e</sup>	a- 5 b- 0.1 c- 1	a- acetone/petroleum ether mixture (1:1, v/v): 10 b- without extraction c- cyclohexane/benzene mixture (1:1, v/v): 2
distilled spirit of barley shochu <sup>10</sup>	269	-	HPLC-MS/MS <sup>f</sup>	200	-
LITERATURE FOR AROMATIC POLYCYCLIC HYDROCARBONS					
sugarcane distilled spirit <sup>7</sup>	16	SPE <sup>g</sup>	HPLC-FLD <sup>h</sup>	12	methanol: 10 isopropanol/ethyl acetate mixture (1:1, v/v): 4
cachaça <sup>11</sup>	16	SPE <sup>g</sup>	GC-MS <sup>i</sup>	50	dichloromethane: 5 methanol: 5 ethyl acetate: 50



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matrix	number of analytes	extraction	analysis method	sample volume (mL)	solvents and total volumes (mL) spent
cachaça <sup>6</sup>	15	SPE <sup>g</sup>	HPLC-FLD <sup>h</sup>	30	dichloromethane: 6 acetonitrile: 15 dichloromethane/hexane mixture (1:1, v/v): 2
cachaça, rum, whiskey and alcohol fuel <sup>12</sup>	15	SPE <sup>g</sup>	HPLC-FLD <sup>h</sup>	30	dichloromethane: 6 acetonitrile: 15 dichloromethane/hexane mixture (1:1, v/v): 2
alcoholic drinks <sup>26</sup>	7	SPE <sup>g</sup> using C18 minicolumns in series	HPLC-FLD <sup>h</sup>	100	methanol: 5 acetonitrile/water mixture (20:80, v/v): 20 hexane: 6
cachaça <sup>27</sup>	1	a- SPE <sup>g</sup> b- LLE <sup>b</sup> with cyclohexane c- LLE with dimethylformamide/water	HPLC-FLD <sup>h</sup>	a- 10 b- 50 c- 20	a- methanol: 10; isopropanol: 1; cyclohexane: 10 b- cyclohexane: 190 c- dimethylformamide-water mixture (9:1, v/v): 100 cyclohexane: 240
cachaça <sup>13</sup>	5	LLE <sup>b</sup>	HPLC-FLD <sup>h</sup> e GC-MS <sup>i</sup>	20	dimethylformamide-water mixture (9:1, v/v): 100 cyclohexane: 240
whisky, gin, rum, brandy and tequila <sup>15</sup>	12	USAEME <sup>j</sup>	GC-MS <sup>i</sup>	5	carbon tetrachloride: 40 µL

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matrix	number of analytes	extraction	analysis method	sample volume (mL)	solvents and total volumes (mL) spent
caçaça <sup>14</sup>	16	DI-CF-SPME <sup>k</sup>	GC-MS <sup>i</sup>		-
DEVELOPED METHOD					
Brazilian caçaça	PAHs: 16 pesticides: 93	modified QuEChERS	GC-MS/MS <sup>a</sup>	20	dichloromethane: 10

<sup>a</sup>GC-MS/MS: Gas Chromatography tandem Mass Spectrometry; <sup>b</sup>LLE: Liquid-Liquid Extraction; <sup>c</sup>GC-NPD: Gas Chromatography with Nitrogen Phosphorous Detector; <sup>d</sup>GC-ECD: Gas Chromatography with Electron Capture Detector; <sup>e</sup>HPLC-UV/vis: High Performance Liquid Chromatography with Ultraviolet/visible Detector; <sup>f</sup>HPLC-MS/MS: High Performance Liquid Chromatography tandem Mass Spectrometry; <sup>g</sup>SPE: Solid-Phase Extraction; <sup>h</sup>HPLC-FLD: High Performance Liquid Chromatography with Fluorescence Detector; <sup>i</sup>GC-MS: Gas Chromatography/ Mass Spectrometry; <sup>j</sup>USAEME: Ultrasound-Assisted Emulsification Microextraction; <sup>k</sup>DI-CF-SPME: Direct Immersion Cold Fiber Mode Solid Phase Microextraction.

**Table S3. Values of  $R^2$ ,  $t_{cal}$  for the Correlation Coefficient,  $F_{lack\ of\ fit}$  and  $F_{sig}$ , on Three Validation Days**

analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
PESTICIDES												
2,4-D	0.98	34.09	3.38	1161.81	0.94	19.18	5,90	367.80	0.94	20.23	2.60	409.31
2,4-DDD	0.90	14.67	1.10	215.75	0.92	16.15	2.25	260.80	0.98	34.66	2.09	1201.09
2,4-DDE	0.96	26.67	0.61	710.99	0.91	15.32	2.65	234.96	0.97	29.75	0.30	885.14
2,4-DDT	0.99	40.93	0.41	1675.01	0.71	7.40	0.38	54.82	0.98	39.83	0.45	1586.64
4,4-DDD	0.96	23.51	1.80	552.64	0.97	25.09	4.79	629.56	0.95	20.78	1.18	431.75
4,4-DDE	0.97	28.35	0.74	803.99	0.82	10.16	0.31	103.27	0.98	37.19	0.40	1383.17
4,4-DDT	0.85	11.26	3.05	126.76	0.87	12.18	0.38	148.38	0.96	22.13	2.95	489.67
acrinathrin	0.98	35.68	1.60	1272.80	0.93	16.58	2.14	274.98	0.99	49.98	1.03	2498.28
alachlor	0.97	29.59	1.66	875.35	0.93	17.09	2.45	292.04	0.99	47.25	0.25	2232.64
aldrin	0.97	26.26	0.47	689.52	0.90	14.59	0.84	212.81	0.96	24.62	0.03	606.24
ametryn	0.99	49.69	0.93	2469.44	0.91	14.60	0.16	213.14	0.99	43.49	1.10	1890.96
azinphos-methyl	0.91	15.45	0.55	238.79	0.91	15.21	0.89	231.49	0.94	19.08	2.79	363.88
azoxystrobin	0.96	24.87	2.12	618.46	0.95	20.59	1.14	423.76	0.99	44.25	0.55	1958.36
benfluralin	0.94	19.47	1.25	378.97	0.91	15.37	0.47	236.12	0.96	23.35	1.25	545.06
bentazone	0.75	8.20	0.21	67.28	0.89	13.36	1.30	178.52	0.97	25.59	8.42	654.60
bifenthrin	0.97	25.38	0.91	644.10	0.98	34.75	1.55	1207.39	0.98	34.41	0.89	1183.74
bromophos-ethyl	0.97	26.44	1.30	699.29	0.91	15.27	1.81	233.28	0.99	43.48	0.81	1890.10

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analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
bromophos-methyl	0.92	16.35	0.12	267.19	0.95	19.45	2.52	378.39	0.98	31.56	0.60	996.23
bromopropylate	0.96	23.57	2.47	555.52	0.99	48.74	1.36	2375.97	0.97	27.31	1.43	745.64
buprofezin	0.98	38.95	0.45	1517.48	0.99	43.58	1.71	1899.10	0.99	52.11	2.58	2715.29
carbofenotion	0.98	37.86	1.48	1433.04	0.78	9.55	0.26	91.26	0.98	37.41	2.16	1399.36
carbofuran	0.97	27.82	1.46	773.85	0.94	18.41	4.22	339.09	0.99	44.47	2.50	1977.70
carboxin	0.97	29.99	2.29	899.59	0.91	14.63	0.84	214.17	0.98	42.72	1.49	1824.61
cyfluthrin	0.96	25.63	0.37	657.00	0.90	14.16	1.56	200.54	0.99	47.33	2.33	2240.52
cinidon-ethyl	0.95	20.88	0.04	436.18	0.83	10.40	0.20	108.17	0.98	39.65	0.89	1571.75
cypermethrin	0.96	24.59	0.32	604.83	0.95	20.53	1.90	421.43	0.99	49.42	1.29	2442.15
cyprodinil	0.98	37.67	1.33	1419.12	0.93	17.15	2.55	294.27	0.98	36.05	1.11	1299.80
chlorbenzylate	0.94	19.08	0.48	364.21	0.94	19.51	2.93	380.50	0.99	46.34	0.52	2147.13
cis-chlordane	0.97	31.32	0.89	981.21	0.94	18.96	2.20	359.52	0.99	51.32	0.62	2633.61
trans- chlordane	0.97	30.41	0.83	924.83	0.95	20.93	1.35	437.99	0.99	47.70	0.19	2275.06
chlorfenapyr	0.97	31.08	0.81	966.22	0.94	17.86	2.95	318.81	0.98	42.12	0.83	1773.86
chlorfenson	0.98	34.55	0.22	1193.51	0.93	17.42	2.70	303.44	0.98	38.29	0.90	1466.18
chlorothalonil	0.95	22.14	0.94	490.10	0.92	16.23	0.98	263.44	0.96	25.09	0.12	629.69
chlorpyrifos	0.96	26.51	0.30	702.65	0.90	14.47	0.25	209.44	0.98	30.41	0.45	924.55
chlorpyrifos-methyl	0.93	18.94	0.59	358.62	0.90	14.45	2.37	208.84	0.97	31.74	1.68	1007.15
coumaphos	0.94	19.21	2.35	369.04	0.94	18.46	2.49	340.69	0.97	26.42	2.32	698.23
deltamethrin	0.95	22.15	0.72	490.81	0.93	16.65	0.71	277.06	0.98	42.63	2.89	1817.36

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analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
dicamba	0.99	44.89	2.24	2015.40	0.90	14.02	1.40	196.67	0.99	56.88	1.71	3234.84
dicloran	0.99	38.76	6.52	1502.48	0.91	15.35	1.90	235.66	0.99	39.28	3.63	1542.80
dichlofluanide	0.95	23.60	0.65	557.17	0.90	14.20	1.07	201.64	0.99	53.80	0.61	2894.85
dichlorvos	0.93	17.18	32.10	295.10	0.91	15.06	1.88	226.92	0.97	25.77	1.18	664.06
dicofol	0.94	19.08	0.48	364.21	0.91	15.02	1.61	225.61	0.98	40.53	1.81	1642.30
disulfoton	0.95	20.06	1.24	402.52	0.93	17.51	0.89	306.68	0.95	22.44	1.27	503.67
disulfoton sulfone	0.92	17.17	1.16	294.83	0.89	13.68	0.85	187.13	0.94	18.78	1.58	352.65
alpha-endosulfan	0.97	29.35	0.36	861.53	0.91	15.01	0.65	225.41	0.99	52.74	0.51	2781.26
endrin	0.91	15.78	1.43	249.03	0.90	14.67	1.59	215.22	0.99	39.93	1.83	1594.59
EPN	0.92	16.24	0.99	263.72	0.92	15.99	0.80	255.64	0.99	39.90	2.91	1592.20
epoxiconazole	0.96	23.62	0.69	557.79	0.84	11.49	0.55	131.94	0.98	37.69	0.50	1420.20
spiroxamine	0.99	42.1599	0.68	1777.45	0.97	24.44	3.93	597.35	0.99	63.26	0.01	4001.95
ethion	0.96	26.89	2.55	723.23	0.92	15.67	1.91	245.41	0.99	42.28	0.85	1787.67
ethoprophos	0.97	25.07	1.71	628.41	0.90	14.27	1.84	203.73	0.94	20.42	1.31	416.98
etrimphos	0.93	17.54	0.83	307.61	0.90	14.28	0.95	204.04	0.98	36.20	0.14	1310.46
fenbuconazole	0.96	23.72	0.85	562.44	0.90	14.29	0.20	204.28	0.99	42.52	0.19	1808.04
fenazaquin	0.98	36.65	1.75	1343.24	0.90	14.79	1.48	218.85	0.97	32.46	0.87	1053.65
fenchlorphos	0.94	20.40	1.24	416.20	0.91	14.54	0.78	211.43	0.96	25.32	0.92	641.30
fenitrothion	0.91	15.67	1.00	245.53	0.91	15.13	0.88	229.03	0.97	27.03	1.48	730.55
fenobucarb	0.91	15.91	0.61	253.11	0.91	15.68	0.76	245.85	0.94	20.59	0.60	424.04

**Table S3. Values of  $R^2$ ,  $t_{cal}$  for the Correlation Coefficient,  $F_{lack\ of\ fit}$  and  $F_{sig}$ , on Three Validation Days**

analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
fenoxaprop-ethyl	0.96	25.92	1.00	671.89	0.90	14.35	1.03	205.89	0.99	45.51	0.52	2071.36
fenvalerate	0.96	25.47	2.45	648.55	0.95	22.16	0.97	490.91	0.98	35.72	1.50	1275.80
fluazifop-p-butyl	0.97	31.20	0.41	973.26	0.94	19.22	1.42	369.53	0.99	50.46	1.73	2546.40
flusilazole	0.97	30.79	0.62	948.32	0.97	25.52	12.81	651.05	0.99	50.67	0.94	2567.51
beta-HCH	0.95	21.23	0.31	450.82	0.92	15.52	0.89	240.80	0.96	25.39	0.01	644.80
gamma-HCH	0.97	32.92	2.41	1083.76	0.96	21.64	4.78	468.39	0.99	48.63	0.81	2364.79
heptachlor	0.94	20.26	0.65	410.63	0.96	24.32	1.31	591.49	0.96	26.62	2.90	708.54
hexazinone	0.96	24.43	0.70	596.63	0.94	20.72	1.28	429.26	0.98	37.86	0.74	1433.20
iprobenfos	0.95	21.48	2.79	461.34	0.94	18.63	0.82	346.92	0.98	33.22	3.93	1103.42
iprodione	0.91	15.01	1.63	225.28	0.98	29.92	1.41	895.36	0.99	43.95	1.93	1931.83
isocarbophos	0.93	16.76	1.88	280.81	0.95	21.12	1.26	445.93	0.99	38.84	6.53	1508.41
isodrin	0.96	24.27	0.37	588.94	0.89	13.50	4.11	182.28	0.99	44.01	0.44	1936.69
isoxaflutole	0.96	26.26	1.55	689.73	0.98	39.52	1.41	1561.67	0.99	43.01	2.33	1849.52
mervinphos	0.91	15.01	0.45	225.20	0.91	15.19	0.30	230.77	0.91	14.76	0.24	217.75
metribuzine	0.97	29.75	1.95	885.26	0.93	18.13	2.96	328.62	0.99	52.34	3.01	2739.68
mirex	0.97	27.94	2.21	780.75	0.92	17.27	0.77	298.13	0.97	28.76	0.25	827.19
oxyfluorfen	0.97	25.64	2.78	657.57	0.90	15.05	0.17	226.36	0.99	49.37	8.19	2437.37
parathion-ethyl	0.93	19.32	2.48	373.41	0.88	12.72	0.78	161.79	0.99	41.74	4.86	1742.53
permethrin	0.92	17.65	1.47	311.37	0.95	24.17	1.00	584.15	0.99	51.83	0.28	2686.21
pirimicarb	0.98	33.11	1.81	1096.20	0.94	19.30	2.89	372.46	0.98	31.85	1.01	1014.56

**Table S3. Values of  $R^2$ ,  $t_{cal}$  for the Correlation Coefficient,  $F_{lack\ of\ fit}$  and  $F_{sig}$ , on Three Validation Days**

analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
pirimiphos-ethyl	0.95	19.54	2.89	381.75	0.94	20.18	1.83	407.03	0.97	29.61	1.32	876.53
pirimiphos-methyl	0.97	30.67	2.97	940.89	0.95	21.87	2.42	478.08	0.97	26.88	0.98	722.36
promecarb	0.97	28.71	1.89	824.52	0.89	14.09	1.94	198.59	0.96	22.38	1.07	500.69
prometryn	0.99	46.67	1.00	2177.68	0.93	18.62	1.58	346.86	0.97	27.94	0.90	780.54
propiconazole	0.98	35.50	0.93	1259.94	0.91	15.18	1.56	230.34	0.96	22.64	1.49	512.68
quintozene	0.96	23.66	1.19	559.64	0.86	11.74	0.48	137.79	0.94	19.30	2.47	372.44
resmethrin	0.93	17.26	2.90	298.04	0.94	19.26	1.26	370.87	0.99	41.32	2.13	1707.16
simazine	0.93	17.30	2.75	299.36	0.93	17.48	0.85	305.64	0.97	29.44	0.60	866.70
tebuconazole	0.96	23.11	1.84	534.23	0.92	15.91	1.74	253.17	0.91	16.09	0.39	258.93
tetraconazole	0.97	28.82	2.32	830.71	0.90	13.91	2.33	193.50	0.96	24.00	2.28	576.02
thiobencarb	0.93	19.62	1.44	384.75	0.92	15.48	2.67	239.72	0.94	19.93	0.96	397.07
tolclofos-methyl	0.95	23.47	2.41	550.81	0.94	18.70	1.66	349.68	0.96	24.91	1.59	620.38
trifluralin	0.96	22.10	1.35	488.27	0.95	20.38	0.56	415.49	0.92	15.80	0.47	249.77
triticonazole	0.97	26.58	1.78	706.59	0.92	16.04	2.43	257.17	0.91	15.56	0.72	242.21
uniconazole-P	0.96	22.98	0.42	527.87	0.98	36.43	0.26	1326.79	0.94	18.32	0.92	335.61
vinclozolin	0.98	35.07	2.45	1230.17	0.94	19.26	0.95	370.77	0.98	34.49	1.50	1189.36
PAHs												
MCH	0.99	58.84	2.04	3462.20	0.93	18.40	1.28	338.40	0.95	20.49	0.77	419.99
BaA	0.99	42.24	1.74	1784.44	0.94	20.51	0.56	420.75	0.98	33.13	2.57	1097.63
BbFA	0.98	31.72	1.05	1006.07	0.95	20.12	2.31	404.84	0.95	21.54	0.73	463.86

**Table S3. Values of  $R^2$ ,  $t_{cal}$  for the Correlation Coefficient,  $F_{lack\ of\ fit}$  and  $F_{sig}$ , on Three Validation Days**

analyte	1st day				2nd Day				3rd day			
	$R^2$ <sup>a</sup>	$t_{cal}$ <sup>b</sup>	$F_A$ <sup>c</sup>	$F_B$ <sup>d</sup>	$R^2$	$t_{cal}$	$F_A$	$F_B$	$R^2$	$t_{cal}$	$F_A$	$F_B$
BjFA	0.98	36.32	0.28	1318.82	0.92	16.92	1.22	286.26	0.97	25.77	2.70	663.91
BkFA	0.87	12.35	0.22	152.45	0.93	19.30	0.37	372.39	0.97	25.96	2.30	674.06
BaP	0.96	24.59	2.32	604.49	0.94	20.24	0.87	409.83	0.96	23.28	1.29	542.08
BghiP	0.93	17.95	1.21	322.19	0.94	19.84	1.32	393.66	0.96	24.59	2.56	604.55
CHR	0.94	18.21	0.22	331.69	0.93	19.03	0.16	362.27	0.97	26.96	0.72	726.84
CPP	0.92	15.46	0.82	239.05	0.99	43.18	1.00	1864.27	0.98	38.04	2.21	1447.40
DBahA	0.93	17.43	0.88	303.86	0.96	24.84	1.53	616.93	0.94	19.72	2.64	388.77
DBaeP	0.94	18.66	2.03	348.04	0.98	34.40	2.47	1183.14	0.97	27.45	2.66	753.77
DBahP	0.92	17.41	0.87	303.27	0.99	42.76	2.93	1828.22	0.97	32.14	1.74	1032.94
DBaiP	0.97	28.02	2.67	785.12	0.97	31.57	2.21	996.55	0.97	27.48	2.30	755.09
DBalP	0.91	14.66	2.90	214.95	0.98	34.16	1.21	1166.85	0.93	18.34	0.48	336.27
IP	0.92	18.17	2.56	330.04	0.96	26.53	2.87	703.80	0.97	26.83	1.50	719.84
BcFL	0.94	18.52	0.14	342.84	0.91	15.83	0.23	250.46	0.97	29.76	0.95	885.75

<sup>a</sup> $R^2$ : determination coefficient; <sup>b</sup> $t_{cal}$ : calculated t-value; <sup>c</sup> $F_{lack\ of\ fit} = F_A$ : F for lack of fit; <sup>d</sup> $F_{sig} = F_B$ : F for goodness of fit.



**Table S4. Average R and RSD Values for Pesticides and PAHs, on the Three Validation Days**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	R <sup>b</sup> (%)	RSD <sup>c</sup> (%)	R (%)	RSD (%)	R (%)	RSD (%)
PESTICIDES						
2,4-D	88.6	15.0	98.2	14.4	93.2	10.3
2,4-DDD	103.9	15.7	102.9	16.2	90.7	18.4
2,4-DDE	94.1	20.2 <sup>d</sup>	100.9	10.6	98.9	12.5
2,4-DDT	93.4	19.1	97.5	9.7	96.2	10.0
4,4-DDD	107.0	16.2	102.1	11.8	101.1	13.4
4,4-DDE	102.5	16.5	95.4	9.3	93.7	10.2
4,4-DDT	100.1	15.6	103.8	18.6	104.1	22.0 <sup>d</sup>
acrinathrin	95.5	14.2	98.7	10.7	97.3	10.2
alachlor	95.4	14.3	101.4	9.7	98.6	7.0
aldrin	98.0	19.1	97.6	12.4	98.7	10.9
ametryn	99.8	11.8	100.1	6.6	95.4	8.0
azinphos-methyl	114.8	13.8	97.4	17.3	103.7	14.8
azoxystrobin	104.6	12.2	102.3	8.9	95.4	12.3
benfluralin	105.4	10.3	93.3	15.2	96.7	13.1
bentazone	112.0	8.6	101.8	14.5	98.1	25.5 <sup>d</sup>
bifenthrin	101.7	11.1	106.0	19.5	97.8	7.9
bromophos-ethyl	103.3	20.0	99.0	16.4	94.4	14.8
bromophos-methyl	98.5	15.4	96.7	10.2	94.7	14.0
bromopropylate	108.6	9.9	103.4	12.5	98.5	9.6
buprofezin	99.8	12.4	102.9	9.5	97.0	7.1
carbofenotion	94.0	17.2	95.4	11.4	96.0	11.2

**Table S4. Average R and RSD Values for Pesticides and PAHs, on the Three Validation Days**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	R <sup>b</sup> (%)	RSD <sup>c</sup> (%)	R (%)	RSD (%)	R (%)	RSD (%)
carbofuran	99.7	15.6	98.1	12.0	106.0	14.0
carboxin	118.2	18.4	99.4	10.2	98.9	9.1
cyfluthrin	100.7	15.0	98.9	11.2	98.4	12.5
cinidon-ethyl	100.1	13.5	98.0	11.9	92.2	14.2
cypermethrin	102.1	16.0	96.0	9.8	96.5	12.6
cyprodinil	88.3	10.0	100.2	12.7	103.3	10.3
chlorbenzylate	99.7	15.2	100.0	9.1	93.6	10.4
cis-chlordane	102.3	16.5	103.2	8.9	98.5	7.0
trans- chlordane	102.7	14.9	102.1	7.5	97.1	8.1
chlorfenapyr	95.7	13.6	101.6	9.9	96.4	10.6
chlorfenson	96.4	19.9	101.9	13.3	95.0	8.6
chlorothalonil	97.7	17.7	96.0	8.5	97.3	10.9
chlorpyrifos	99.3	22.6 <sup>d</sup>	96.9	10.0	97.5	8.8
chlorpyrifos-methyl	100.4	15.7	93.9	13.2	94.8	15.1
coumaphos	113.3	9.3	96.0	13.8	96.3	12.5
deltamethrin	99.3	15.7	98.2	13.3	95.4	13.7
dicamba	101.3	17.8	99.6	12.2	99.9	19.1
dicloran	108.2	6.7	94.1	11.4	95.4	10.0
dichlofluanide	102.2	14.6	105.0	9.3	96.3	11.2
dichlorvos	102.3	16.2	104.1	14.1	101.9	11.3
dicofol	102.8	15.7	102.3	11.5	99.9	12.2
disulfoton	147.5 <sup>d</sup>	43.0 <sup>d</sup>	93.4	20.0	97.6	12.3
disulfoton sulfone	105.6	8.3	94.2	12.2	95.5	12.5
alpha-endosulfan	101.3	16.6	101.07	8.9	99.3	10.1

**Table S4. Average R and RSD Values for Pesticides and PAHs, on the Three Validation Days**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	R <sup>b</sup> (%)	RSD <sup>c</sup> (%)	R (%)	RSD (%)	R (%)	RSD (%)
endrin	104.1	13.5	100.9	10.0	96.6	12.8
EPN	103.0	12.0	101.3	10.7	98.5	14.1
epoxiconazole	112.2	8.0	94.6	18.1	94.6	13.8
spiroxamine	103.1	9.9	102.7	9.0	94.2	12.6
ethion	103.9	15.2	100.3	9.1	98.8	12.3
ethoprophos	108.2	14.1	104.2	20.8 <sup>d</sup>	98.4	15.4
etrimphos	106.4	15.1	98.2	12.0	94.5	10.3
fenbuconazole	108.3	7.6	100.1	14.9	97.5	16.6
fenazaquin	97.6	15.3	98.3	11.9	95.7	10.3
fenchlorphos	99.8	19.6	98.0	14.1	94.6	11.1
fenitrothion	110.2	11.9	97.6	8.6	93.3	11.1
fenobucarb	93.2	17.1	86.7	15.3	95.7	11.7
fenoxaprop-ethyl	98.7	17.6	100.8	10.9	95.6	10.9
fenvalerate	93.8	15.8	98.2	12.1	93.1	13.6
fluazifop-p-butyl	97.2	17.5	102.1	8.2	96.5	8.4
flusilazole	104.6	11.1	102.2	7.7	94.5	11.8
beta-HCH	91.4	16.1	96.8	16.7	98.9	10.6
gamma-HCH	95.3	13.1	100.1	6.5	98.8	7.5
heptachlor	94.2	11.6	94.0	15.4	94.9	7.4
hexazinone	101.7	14.5	107.0	19.2	95.2	10.2
iprobenfos	110.5	12.4	105.4	15.3	96.7	12.7
iprodione	107.0	14.3	94.0	17.9	94.9	17.0
isocarbophos	111.2	15.1	93.8	18.9	95.4	14.6
isodrin	102.0	17.7	94.7	9.3	93.8	12.7

**Table S4. Average R and RSD Values for Pesticides and PAHs, on the Three Validation Days**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	R <sup>b</sup> (%)	RSD <sup>c</sup> (%)	R (%)	RSD (%)	R (%)	RSD (%)
isoxaflutole	99.7	14.4	96.0	10.1	99.4	11.8
mervinphos	110.4	14.4	96.8	18.9	90.5	17.1
metribuzine	102.2	10.9	95.7	12.3	99.6	16.5
mirex	100.8	17.6	101.4	8.5	99.6	11.7
oxyfluorfen	104.9	12.8	97.1	14.2	97.3	16.9
parathion-ethyl	106.2	11.5	97.6	10.5	97.7	12.5
permethrin	94.7	15.2	100.4	10.9	90.2	15.6
pirimicarb	99.1	13.4	104.5	8.3	97.1	9.9
pirimiphos-ethyl	96.4	12.0	100.6	10.4	99.9	10.0
pirimiphos-methyl	99.4	15.5	100.1	6.1	101.8	9.0
promecarb	100.1	14.5	94.9	13.0	100.4	12.6
prometryn	99.9	15.7	105.4	6.5	98.2	10.5
propiconazole	96.5	18.8	101.6	14.0	104.8	12.2
quintozene	112.6	9.5	90.1	15.7	100.0	14.2
resmethrin	98.3	17.8	103.5	17.8	97.4	11.9
simazine	101.8	11.8	107.4	15.3	97.7	14.0
tebuconazole	102.3	14.3	112.7	13.7	98.1	17.0
tetraconazole	96.5	16.7	104.2	10.3	102.8	11.9
thiobencarb	93.3	19.1	96.6	13.2	101.4	9.8
tolclofos-methyl	100.1	18.0	98.1	8.2	102.0	9.5
trifluralin	94.8	19.9	90.3	13.9	102.0	14.5
triticonazole	90.6	9.4	107.7	14.6	100.5	12.8
uniconazole-P	88.8	16.5	111.0	32.6 <sup>d</sup>	105.3	16.4
vinclozolin	94.27	14.7	100.4	6.9	105.2	12.2

**Table S4. Average R and RSD Values for Pesticides and PAHs, on the Three Validation Days**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	R <sup>b</sup> (%)	RSD <sup>c</sup> (%)	R (%)	RSD (%)	R (%)	RSD (%)
PAHs						
MCH	120.8 <sup>d</sup>	18.7	95.28	14.3	97.3	22.4
BaA	95.2	25.3	93.10	15.5	90.5	11.0
BbFA	97.7	27.3	98.63	14.7	92.7	10.1
BjFA	104.4	22.0	92.47	17.3	92.4	9.4
BkFA	110.1	19.3	95.07	16.5	90.7	12.0
BaP	87.8	18.1	93.70	15.0	87.7	11.8
BghiP	92.5	16.0	96.48	10.8	90.8	8.4
CHR	111.5	22.6	87.08	15.8	84.8	9.8
CPP	107.5	23.4	94.73	6.2	92.1	10.5
DBahA	96.4	18.9	93.88	14.8	89.4	11.7
DBaeP	95.3	17.3	97.32	14.9	91.7	17.7
DBahP	108.1	18.0	96.42	16.2	99.0	9.3
DBaiP	89.5	16.3	97.68	12.7	95.7	11.4
DBalP	102.8	12.1	96.10	13.9	95.6	11.3
IP	92.6	17.1	98.56	7.0	97.8	6.6
BcFL	99.4	17.1	96.26	11.5	95.4	10.4

<sup>a</sup>Level 1: 0.01 mg L<sup>-1</sup>, level 2: 0.05 mg L<sup>-1</sup> and level 3: 0.10 mg L<sup>-1</sup>, for pesticides; level 1: 0.001 mg L<sup>-1</sup>, level 2: 0.005 mg L<sup>-1</sup> and level 3: 0.010 mg L<sup>-1</sup>, for PAHs; <sup>b</sup>R: recovery; <sup>c</sup>RSD: relative standard deviation; <sup>d</sup>Values were disregarded for not meeting the minimum criteria of acceptability.

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
PESTICIDES						
2,4-D	0.0035	67	0.0034	13	0.0066	13
2,4-DDD	0.0035	70	0.0029	12	0.0058	12
2,4-DDE	0.0028	57	0.0032	13	0.0057	11
2,4-DDT	0.0021	42	0.0025	10	0.0071	14
4,4-DDD	0.0029	59	0.0023	9	0.0045	9
4,4-DDE	0.0020	40	0.0025	10	0.0062	12
4,4-DDT	0.0033	66	0.0043	17	0.0127	25
acrinathrin	0.0022	44	0.0018	7	0.0034	7
alachlor	0.0023	47	0.0026	10	0.0047	9
aldrin	0.0040	80	0.0036	15	0.0080	16

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
ametryn	0.0014	27	0.0020	8	0.0054	11
azinphos-methyl	0.0030	60	0.0027	11	0.0048	10
azoxystrobin	0.0040	80	0.0036	15	0.0080	16
benfluralin	0.0022	44	0.0022	9	0.0039	8
bentazone	0.0036	72	0.0028	11	0.0072	14
bifenthrin	0.0021	42	0.0032	13	0.0042	8
bromophos-ethyl	0.0026	51	0.0025	10	0.0044	9
bromophos-methyl	0.0020	41	0.0017	7	0.0040	8
bromopropylate	0.0021	43	0.0020	8	0.0032	7
buprofezin	0.0013	26	0.0014	6	0.0022	4
carbofenotion	0.0023	45	0.0019	8	0.0036	7
carbofuran	0.0040	80	0.0036	15	0.0080	16
carboxin	0.0022	43	0.0018	7	0.0032	6

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
cyfluthrin	0.0040	80	0.0036	15	0.0080	16
cinidon-ethyl	0.0013	26	0.0016	6	0.0036	7
cypermethrin	0.0020	37	0.0017	7	0.0037	7
cyprodinil	0.0024	49	0.0026	11	0.0054	11
chlorbenzylate	0.0040	80	0.0036	15	0.0080	16
cis-chlordane	0.0020	40	0.0016	6	0.0027	5
trans- chlordane	0.0015	31	0.0013	5	0.0025	5
chlorfenapyr	0.0023	45	0.0018	7	0.0035	7
chlorfenson	0.0021	42	0.0020	8	0.0030	6
chlorothalonil	0.0019	38	0.0015	6	0.0033	7
chlorpyrifos	0.0014	27	0.0014	6	0.0025	5
chlorpyrifos-methyl	0.0030	60	0.0024	10	0.0048	10
coumaphos	0.0040	80	0.0036	15	0.0080	16



**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
deltamethrin	0.0020	40	0.0020	8	0.0039	8
dicamba	0.0022	44	0.0020	8	0.0051	10
dicloran	0.0029	59	0.0022	9	0.0040	8
dichlofluanide	0.0021	42	0.0017	7	0.0035	7
dichlorvos	0.0051	102	0.0035	14	0.0061	12
dicofol	0.0025	50	0.0020	8	0.0040	8
disulfoton	0.0028	57	0.0030	12	0.0041	8
disulfoton sulfone	0.0040	80	0.0036	15	0.0080	16
alpha-endosulfan	0.0015	31	0.0014	5	0.0029	6
endrin	0.0031	62	0.0022	9	0.0045	9
EPN	0.0023	47	0.0019	8	0.0042	8
epoxiconazole	0.0020	47	0.0030	10	0.0039	10
spiroxamine	0.0017	34	0.0016	6	0.0043	9

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
ethion	0.0026	51	0.0019	8	0.0040	8
ethoprophos	0.0031	61	0.0031	12	0.0049	10
etrimphos	0.0021	43	0.0019	8	0.0033	7
fenbuconazole	0.0014	28	0.0022	9	0.0061	12
fenazaquin	0.0024	48	0.0020	8	0.0036	7
fenchlorphos	0.0025	50	0.0022	9	0.0037	8
fenitrothion	0.0027	54	0.0019	8	0.0039	8
fenobucarb	0.0025	50	0.0024	9	0.0038	8
fenoxaprop-ethyl	0.0021	42	0.0018	7	0.0034	7
fenvalerate	0.0022	44	0.0020	8	0.0040	8
fluazifop-p-butyl	0.0018	36	0.0014	6	0.0027	6
flusilazole	0.0023	46	0.0017	7	0.0037	8
beta-HCH	0.0015	30	0.0022	9	0.0030	6

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
gamma-HCH	0.0024	49	0.0017	7	0.0032	6
heptachlor	0.0023	47	0.0023	9	0.0031	6
hexazinone	0.0019	37	0.0025	10	0.0031	6
iprobefos	0.0028	57	0.0025	10	0.0043	9
iprodione	0.0023	46	0.0025	10	0.0047	9
isocarbophos	0.0027	54	0.0028	11	0.0045	9
isodrin	0.0031	62	0.0027	11	0.0060	12
isoxaflutole	0.0017	34	0.0016	6	0.0033	7
mervinphos	0.0021	42	0.0026	10	0.0046	9
metribuzine	0.0026	51	0.0021	9	0.0048	10
mirex	0.0019	38	0.0015	6	0.0034	7
oxyfluorfen	0.0020	41	0.0021	8	0.0046	9
parathion-ethyl	0.0028	56	0.0027	11	0.0072	14

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
permethrin	0.0020	40	0.0018	7	0.0043	9
pirimicarb	0.0025	50	0.0020	8	0.0039	8
pirimiphos-ethyl	0.0029	59	0.0022	9	0.0040	8
pirimiphos-methyl	0.0026	51	0.0019	8	0.0039	8
promecarb	0.0033	66	0.0028	11	0.0052	10
prometryn	0.0021	42	0.0017	7	0.0036	7
propiconazole	0.0028	56	0.0024	9	0.0041	8
quintozene	0.0029	58	0.0026	10	0.0046	9
resmethrin	0.0031	63	0.0028	11	0.0044	9
simazine	0.0030	60	0.0026	10	0.0046	9
tebuconazole	0.0031	61	0.0025	10	0.0052	10
tetraconazole	0.0036	72	0.0027	11	0.0055	11
thiobencarb	0.0031	63	0.0027	11	0.0056	11

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
tolclofos-methyl	0.0028	56	0.0022	9	0.0043	9
trifluralin	0.0023	45	0.0021	9	0.0042	8
triticonazole	0.0033	67	0.0040	16	0.0088	18
uniconazole-P	0.0017	33	0.0041	17	0.0053	11
vinclozolin	0.0040	80	0.0036	15	0.0080	16
PAHs						
MCH	0.00021	42	0.00021	9	0.00057	12
BaA	0.00020	41	0.00022	9	0.00033	7
BbFA	0.00025	49	0.00023	9	0.00035	7
BjFA	0.00024	47	0.00025	10	0.00034	7
BkFA	0.00022	44	0.00023	9	0.00037	7
BaP	0.00026	53	0.00024	10	0.00040	8
BghiP	0.00031	61	0.00023	9	0.00039	8

**Table S5.  $u_{comb}$  and U Values for Pesticides and PAHs**

analyte	level 1 <sup>a</sup>		level 2 <sup>a</sup>		level 3 <sup>a</sup>	
	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)	$u_{comb}^b$ (mg L <sup>-1</sup> )	U <sup>c</sup> (%)
CHR	0.00015	31	0.00021	8	0.00028	6
CPP	0.00021	41	0.00014	6	0.00033	7
DBahA	0.00030	61	0.00025	10	0.00043	9
DBaeP	0.00028	57	0.00025	10	0.00052	10
DBahP	0.00023	46	0.00024	10	0.00033	7
DBaiP	0.00026	51	0.00022	9	0.00039	8
DBalP	0.00028	55	0.00023	9	0.00040	8
IP	0.00026	63	0.00021	8	0.00038	8
BcFL	0.00015	29	0.00016	6	0.00029	6

<sup>a</sup>Level 1: 0.01 mg L<sup>-1</sup>, level 2: 0.05 mg L<sup>-1</sup> and level 3: 0.10 mg L<sup>-1</sup>, for pesticides; level 1: 0.001 mg L<sup>-1</sup>, level 2: 0.005 mg L<sup>-1</sup> and level 3: 0.010 mg L<sup>-1</sup>, for PAHs; <sup>b</sup> $u_{comb}$ : combined standard uncertainty of the measurement; <sup>c</sup>U: relative expanded uncertainty.