

**SIMULTANEOUS DETERMINATION OF SELECTED PESTICIDES AND/OR THEIR  
METABOLITES IN URINE BY OFF-LINE SOLID PHASE EXTRACTION AND ULTRA  
HIGH PERFORMANCE LIQUID CHROMATOGRAPHY / HYBRID QUADRUPOLE  
TIME-OF-FLIGHT MASS SPECTROMETRY**

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Electronic supplementary material (11 pages) contains the following Tables:

- S1. Recovery rates obtained with Phenomenex Strata-X and Waters Oasis HLB cartridges on Evian water spiked at  $10 \mu\text{g.L}^{-1}$  at pH 2 and 7 ( $n = 3$  for each condition) (cartridges were conditioned with successively 10 mL of a 60% DCM / 40% ACN mixture, 10 mL of MeOH and 10 mL of ultra-pure water at pH 2 or 7, and analytes eluted with 10 mL of a 60% DCM / 40% ACN mixture).
- S2. Recovery rates obtained with Phenomenex Strata-X-AW and Waters Oasis Wax cartridges on Evian water spiked at  $1 \mu\text{g.L}^{-1}$  with and without MeOH washing step ( $n = 3$  for each condition) (cartridges were conditioned with successively 10 mL of a 60% DCM / 40% ACN mixture, 10 mL of MeOH and 10 mL of ultra-pure water at pH 2 or 7, and analytes eluted with 10 mL of a 60% DCM / 40% ACN mixture).
- S3. Spiking experiments on three urine pools (pools #1, #2 and #3) non-spiked and spiked at an intermediate level, method n°1 (ESI-).
- S4. Spiking experiments on two urine pools (pools #2 and #3) non-spiked and spiked at an intermediate level, method n°2 (ESI+).

- S5. Study of the impact of the enzymatic hydrolysis: experiments on two urine pools (pools #1 and #2) non-spiked with and without enzymatic hydrolysis and spiked at an intermediate level with enzymatic hydrolysis, method n°1 (ESI-).
- S6. Study of the impact of thawing/freezing cycles on the conservation of the target substances: experiments on two urine pools (pools #1 and #3) spiked at an intermediate level.
- S7. Pesticide concentrations in fifteen human urine samples, method n°1 (ESI-).
- S8. Pesticide concentrations in fifteen human urine samples, method n°2 (ESI+).

**Table S1**

Recovery rates obtained with Phenomenex Strata-X and Waters Oasis HLB cartridges on Evian water spiked at 10 µg.L<sup>-1</sup> at pH 2 and 7 (n = 3 for each condition) (cartridges were conditioned with successively 10 mL of a 60% DCM / 40% ACN mixture, 10 mL of MeOH and 10 mL of ultra-pure water at pH 2 or 7, and analytes eluted with 10 mL of a 60% DCM / 40% ACN mixture).

Compound <sup>a</sup>	Recovery rate (%) (RSD <sup>b</sup> (%))			
	Strata-X, pH 7	Oasis HLB, pH 7	Strata-X, pH 2	Oasis HLB, pH 2
DMTP	<5	<5	11 (18)	10 (13)
DMDTP	<5	<5	<5	<5
ADHP	6 (7)	10 (5)	<5	<5
DEP	<5	<5	18 (12)	48 (15)
Nicotine	69 (10)	48 (35)	<5	<5
Cotinine	89 (1)	77 (6)	<5	<5
DETP	5 (41)	<5	10 (22)	17 (60)
IMPy	80 (5)	60 (18)	24 (12)	33 (10)
Carbendazim	84 (7)	64 (22)	88 (7)	95 (5)
2-(4-Hydroxyphenoxy)propanoic acid	<5	<5	56 (8)	59 (29)
3-Chloroaniline	119 (2)	56 (4)	73 (30)	57 (36)
6-Chloronicotinic acid	<5	<5	68 (16)	70 (21)
Dimethoate	84 (3)	64 (9)	82 (8)	89 (7)
Methyl-2-(2-hydroxyphenyl)-3-methylacrylate	15 (35)	<5	69 (7)	74 (3)
2-Methyl-6-ethylaniline	118 (2)	56 (9)	102 (9)	61 (43)
Carbofuran phenol	49 (65)	21 (23)	83 (16)	41 (27)
Dichlorvos	63 (7)	<5	92 (8)	53 (42)
3,5-Dichloroaniline	90 (4)	18 (112)	64 (31)	45 (36)
2-Phenylphenol	83 (10)	<5	72 (33)	35 (54)
TCPy	<5	<5	65 (6)	49 (38)
Malathion	93 (9)	<5	109 (32)	70 (24)
Fluazifop (free acid)	<5	<5	99 (8)	109 (2)
Azoxystrobin	103 (5)	22 (142)	140 (15)	137 (20)
DCCA	<5	<5	57 (14)	40 (42)
3PBA	<5	<5	74 (11)	51 (21)
4F3PBA	<5	<5	71 (11)	49 (23)
2,4,6-T	<5	<5	74 (24)	65 (32)
Bromoxynil	<5	<5	70 (11)	57 (25)
Acetochlor	89 (5)	27 (113)	76 (13)	70 (11)
Phorate	53 (9)	7 (48)	29 (42)	13 (19)
Chlorpyrifos-methyl	51 (10)	<5	25 (71)	6 (24)
Quizalofop (free acid)	<5	<5	93 (14)	77 (31)
Chlorpyrifos-ethyl	58 (38)	<5	17 (78)	<5

<sup>a</sup> Compounds listed in order of retention times; <sup>b</sup> n = 3

**Table S2**

Recovery rates obtained with Phenomenex Strata-X-AW and Waters Oasis Wax cartridges on Evian water spiked at 1 µg.L<sup>-1</sup> with and without MeOH washing step (n = 3 for each condition) (cartridges were conditioned with successively 10 mL of a 60% DCM / 40% ACN mixture, 10 mL of MeOH and 10 mL of ultra-pure water at pH 2 or 7, and analytes eluted with 10 mL of a 60% DCM / 40% ACN mixture).

Compound <sup>a</sup>	Recovery rate (%) (RSD <sup>b</sup> (%))			
	Oasis WAX w/o MeOH wash	Oasis WAX w/ MeOH wash	Strata-X-AW w/o MeOH wash	Strata-X-AW w/ MeOH wash
DMP	2 (53)	1 (5)	3 (5)	2 (13)
DMTP	29 (71)	13 (8)	30 (5)	30 (2)
DEP	32 (75)	16 (2)	11 (12)	10 (16)
DETP	79 (10)	61 (15)	68 (14)	76 (8)
2-(4-Hydroxyphenoxy)propanoic acid	16 (61)	50 (56)	88 (4)	84 (8)
6-Chloronicotinic acid	78 (2)	44 (26)	89 (8)	96 (2)
Bromoxynil	34 (99)	47 (1)	87 (8)	94 (2)
TCPy	43 (78)	42 (8)	100 (10)	100 (4)
2,4,6-T	62 (26)	77 (6)	87 (8)	94 (4)
DCCA	60 (34)	<5	86 (9)	86 (3)
Fluazifop (free acid)	57 (31)	53 (12)	75 (8)	82 (0)
3PBA	30 (98)	12 (4)	84 (12)	92 (6)
4F3PBA	32 (98)	14 (10)	95 (3)	104 (4)
Quizalofop (free acid)	28 (100)	49 (6)	81 (11)	84 (4)

<sup>a</sup> Compounds listed in order of retention times; <sup>b</sup> n = 3

**Table S3**

Spiking experiments on three urine pools (pools #1, #2 and #3) non-spiked and spiked at an intermediate level, method n°1 (ESI-).

Compound <sup>a</sup>	Theoretical concentrations ( $\mu\text{g L}^{-1}$ )	Measured concentrations ( $\mu\text{g L}^{-1}$ )																			n	Mean	RSD (%)	Measured/theoretical (%)	
		QC #1 Pool #3	QC #2 Pool #3	QC #3 Pool #3	QC #4 Pool #1	QC #5 Pool #3	QC #6 Pool #1	QC #7 Pool #2	QC #8 Pool #3	QC #9 Pool #3	QC #10 Pool #3	QC #11 Pool #2	QC #12 Pool #3	QC #13 Pool #2	QC #14 Pool #3	QC #15 Pool #2	QC #16 Pool #3	QC #17 Pool #2	QC #18 Pool #3	QC #19 Pool #3	QC #20 Pool #2				
DMP	10	7.95	10.4	8.31	16.4	8.35	8.95	9.10	7.00	9.15	10.3	4.05	9.67	4.68	9.88	9.54	9.05	10.3	9.34	7.05	7.10	20	8.83	28	88
DMTP	10	10.8	9.38	9.78	7.46	10.8	5.08	8.20	8.92	9.17	7.71	7.05	10.0	12.0	8.82	5.75	12.4	10.7	10.3	9.87	7.35	20	9.08	21	91
DEP	10	n.r.	12.6	13.1	11.8	9.93	n.r.	15.5	11.5	13.6	12.0	13.9	13.6	8.52	9.64	12.1	12.8	11.5	10.8	11.5	14.2	18	12.1	14	121
DMDTP	4	4.11	3.57	3.76	3.99	3.98	4.16	4.66	4.41	3.76	3.61	4.42	3.96	3.71	3.71	3.82	4.97	4.26	3.99	4.37	4.42	20	4.08	9	102
DET <sup>b</sup>	2	2.18	2.13	1.82	3.91	2.29	0.852	2.35	2.07	2.19	1.70	2.11	2.18	2.07	2.12	2.04	2.52	2.87	1.86	1.99	2.07	20	2.17	26	108
2-(4-Hydroxyphenoxy)propanoic acid	2	2.04	2.29	2.39	1.76	1.59	1.53	1.93	1.73	1.52	1.87	1.79	2.23	2.20	2.06	1.91	2.34	2.66	1.66	1.81	1.43	20	1.94	17	97
6-Chloronicotinic acid	2	1.99	1.93	1.94	2.12	2.09	2.13	1.95	1.81	1.94	1.96	1.93	1.93	1.99	2.20	2.07	2.56	2.38	1.96	1.84	1.96	20	2.03	9	102
Bromoxynil	0,5	0.522	0.564	0.533	0.534	0.613	0.485	0.491	0.462	0.544	0.579	0.548	0.429	0.423	0.481	0.619	0.707	0.629	0.465	0.507	0.494	20	0.532	14	106
TCPy	2	n.r.	1.63	2.04	1.69	1.95	2.16	2.41	1.81	1.58	2.40	1.57	1.78	1.74	3.45	2.08	2.27	2.03	1.97	2.21	1.02	19	1.99	25	99
2,4,6-T	1	0.647	0.805	0.716	1.06	0.713	1.12	1.23	0.723	0.720	0.517	0.706	0.832	0.971	0.707	0.893	0.891	1.27	0.752	0.611	1.17	20	0.852	25	85
DCCA	10	9.54	12.9	10.9	9.75	10.8	9.36	11.5	10.8	7.29	11.4	11.6	9.65	8.66	10.7	11.9	12.9	11.5	8.79	9.97	11.4	20	10.6	14	106
Fluazifop (free acid)	0,5	0.484	0.454	0.440	0.350	0.533	0.298	0.349	0.436	0.419	0.357	0.327	0.493	0.401	0.545	0.375	0.753	0.363	0.604	0.433	0.390	20	0.440	24	88
3PBA	2	1.89	2.59	2.04	2.18	2.15	2.33	1.92	1.76	1.88	1.81	2.31	1.44	1.80	2.33	1.95	2.16	2.09	1.81	2.28	2.22	20	2.05	13	102
4F3PBA	1	0.941	n.r.	n.r.	0.967	1.09	1.20	0.898	1.03	0.912	1.12	0.975	0.987	1.02	0.872	0.847	1.09	0.944	0.966	0.914	0.960	18	0.985	9	98
Quizalofop (free acid)	0,5	0.509	0.509	0.534	0.586	0.540	0.374	0.459	0.421	0.487	0.429	0.399	0.512	0.468	0.509	0.503	0.610	0.630	0.518	0.443	0.475	20	0.496	13	99

<sup>a</sup>n.r., not reported; <sup>b</sup>Compounds listed in order of retention times.

**Table S4**

Spiking experiments on two urine pools (pools #2 and #3) non-spiked and spiked at an intermediate level, method n°2 (ESI+).

Compound <sup>a</sup>	Theoretical concentrations ( $\mu\text{g.L}^{-1}$ )	Measured concentrations ( $\mu\text{g.L}^{-1}$ )																	n	Mean	RSD (%)	Measured/theoretical (%)
		QC #1 Pool #2	QC #2 Pool #3	QC #3 Pool #2	QC #4 Pool #3	QC #5 Pool #2	QC #6 Pool #3	QC #7 Pool #2	QC #8 Pool #3	QC #9 Pool #2	QC #10 Pool #2	QC #11 Pool #3	QC #12 Pool #2	QC #13 Pool #3	QC #14 Pool #2	QC #15 Pool #3	QC #16 Pool #2	QC #17 Pool #3				
Nicotine	16	17.7	n.r.	15.6	n.r.	17.8	n.r.	15.8	n.r.	13.8	14.1	n.r.	16.7	n.r.	14.3	n.r.	15.9	n.r.	9	15.7	9	98
ADHP	4.0	7.49	6.71	6.73	2.49	6.16	1.78	3.21	2.19	4.39	5.68	3.55	3.18	2.73	3.81	1.51	2.79	2.06	17	3.91	49	98
Cotinine	8.0	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.				
Carbendazim	0.80	0.648	0.699	0.744	0.665	0.838	0.767	0.867	0.723	0.836	0.759	0.796	0.802	0.768	0.676	0.593	0.684	0.739	17	0.741	10	93
IMPy	1.6	1.79	1.12	1.87	1.13	1.68	1.13	1.86	1.24	1.93	1.76	1.37	1.69	1.17	1.62	1.14	1.59	1.27	17	1.49	20	93
Dimethoate	0.80	0.627	0.754	0.607	0.711	0.518	0.708	0.918	0.710	0.972	0.736	0.741	0.777	0.732	0.61	0.749	0.646	0.712	17	0.719	15	90
3-Chloraniline	4.0	3.90	4.44	5.03	3.75	4.36	3.52	3.23	4.34	3.96	4.94	4.14	4.55	4.64	5.22	4.41	4.80	3.99	17	4.31	13	108
Methyl-2-(2-hydroxyphenyl)-3-methylacrylate	32	18.9	50.3	23.1	60.3	28.2	50.6	34.6	49.0	31.4	28.8	56.8	32.4	56.4	29.4	45.4	25.8	54.1	17	39.7	34	124
Dichlorvos	8.0	7.73	7.33	7.75	8.08	7.26	8.82	7.57	8.06	6.23	8.11	10.39	8.11	7.61	7.86	8.71	7.81	8.47	17	7.99	11	100
2-Methyl-6-ethylaniline	4.0	3.74	3.53	3.87	5.05	4.25	3.92	4.12	3.96	4.18	4.65	4.30	4.45	4.49	5.01	4.23	4.41	4.61	17	4.28	10	107
Carbofuran	0.80	2.19	2.71	1.22	1.48	0.837	1.30	1.13	1.33	1.05	1.08	1.70	0.985	1.32	0.905	1.23	0.985	1.34	17	1.34	36	168
Carbofuran phenol	64	206	374	263	554	185	322	246	352	205	366	565	305	502	207	423	215	392	17	334	37	522
DCPU	4.0	2.66	5.17	2.62	4.56	3.61	6.00	4.44	6.32	4.27	3.45	5.47	4.02	7.53	3.79	4.43	4.01	5.39	17	4.57	28	114
Fenpropimorph	1.6	2.85	3.79	2.54	1.51	3.48	4.29	2.03	2.69	2.23	1.99	1.68	1.03	2.53	2.36	2.07	2.33	2.54	17	2.47	33	154
IPPMU	1.6	1.51	2.17	1.39	1.85	1.47	1.96	1.72	1.76	1.60	1.50	2.18	1.60	2.33	1.70	1.81	1.60	2.32	17	1.79	17	112
DCPMU	1.6	1.25	1.85	0.991	1.29	1.45	1.97	1.61	1.76	1.40	1.47	1.63	1.21	1.89	1.65	1.32	1.53	1.73	17	1.53	18	96
Isoproturon	1.6	1.41	1.82	1.41	1.63	1.45	1.65	1.52	1.64	1.44	1.27	1.60	1.37	1.67	1.32	2.02	1.44	1.81	17	1.56	13	97
3,5-Dichloraniline	8.0	9.69	7.37	10.5	5.75	11.1	6.52	7.00	6.32	8.38	9.83	4.84	8.81	6.52	9.16	3.64	9.78	4.74	17	7.64	29	96
2-Phenylphenol	400	385	407	281	302	369	526	441	702	503	594	241	418	724	491	373	284	502	17	444	32	111
Azoxystrobin	0.32	0.300	0.261	0.328	0.303	0.319	0.300	0.352	0.292	0.290	0.301	0.308	0.307	0.258	0.296	0.286	0.315	0.357	17	0.304	9	95
Chlorpropham	1.6	1.41	1.01	1.32	1.07	1.85	1.09	1.73	1.41	1.61	1.42	0.763	1.48	1.32	1.58	0.917	1.49	1.33	17	1.34	22	84
Malathion	0.32	0.354	0.298	0.297	0.320	0.402	0.285	0.307	0.307	0.322	0.337	0.306	0.341	0.337	0.279	0.287	0.305	0.347	17	0.319	10	100
Iprodione	1.6	1.64	1.24	1.44	1.31	1.45	1.57	1.34	1.04	1.57	1.38	1.82	1.08	1.14	1.55	1.45	1.38	1.36	17	1.40	15	87
Acetochlor	0.80	0.714	0.603	0.759	0.670	0.904	0.690	0.848	0.737	0.799	0.696	0.638	0.704	0.716	0.739	0.561	0.609	0.688	17	0.71	12	89
Phorate	1.6	1.56	1.75	1.49	1.54	1.69	1.63	1.81	1.55	1.60	1.78	1.48	1.92	1.92	1.60	2.06	1.44	1.73	17	1.68	10	105
Chlorpyrifos-methyl	1.6	1.48	1.83	1.66	2.19	1.57	2.26	1.32	1.66	1.49	1.66	2.21	1.71	1.93	1.79	1.81	1.54	1.46	17	1.74	16	109
Chlorpyrifos-ethyl	1.6	1.54	1.76	1.92	0.977	1.65	1.69	1.63	1.49	1.87	1.33	1.29	1.47	2.24	1.34	1.64	1.61	1.53	17	1.59	18	99

n.r., not reported; <sup>a</sup> Compounds listed in order of retention times.

**Table S5**

Study of the impact of the enzymatic hydrolysis: experiments on two urine pools (pools #1 and #2) non-spiked with and without enzymatic hydrolysis and spiked at an intermediate level with enzymatic hydrolysis, method n°1 (ESI-).

Compound <sup>a</sup>	Theoretical concentrations ( $\mu\text{g.L}^{-1}$ )	Measured concentrations ( $\mu\text{g.L}^{-1}$ )									
	Pool #1					Pool #2					
	w/o EH non-spiked	w/ EH non-spiked	$\Delta C$ (%)	w/ EH spiked	Measured /theoretical (%)	w/o EH non-spiked	w/ EH non-spiked	$\Delta C$ (%)	w/ EH spiked	Measured /theoretical (%)	
<b>DMP</b>	25	4.95	6.07	<b>23</b>	29.17	<b>92</b>	6.52	4.77	<b>-27</b>	25.08	<b>81</b>
<b>DMTP</b>	25	4.13	4.80	<b>16</b>	33.27	<b>114</b>	3.15	3.39	<b>8</b>	28.58	<b>101</b>
<b>DEP</b>	5	16.28	14.26	<b>-12</b>	24.15	<b>198</b>	5.68	4.19	<b>-26</b>	16.75	<b>251</b>
<b>DMDTP</b>	10	0.90	0.83	<b>-8</b>	11.17	<b>103</b>	0.27	0.31	<b>14</b>	10.00	<b>97</b>
<b>DETP</b>	5	5.79	5.82	<b>1</b>	11.70	<b>118</b>	1.33	1.29	<b>-3</b>	6.99	<b>114</b>
<b>2-(4-Hydroxyphenoxy)propanoic acid</b>	5	0.19	0.20	<b>6</b>	4.17	<b>79</b>	0.22	0.24	<b>7</b>	4.66	<b>88</b>
<b>6-Chloronicotinic acid</b>	5	<0.13	<0.13	-	5.30	<b>106</b>	<0.13	<0.13	-	5.03	<b>101</b>
<b>Bromoxynil</b>	1.25	<0.031	<0.031	-	1.31	<b>105</b>	<0.031	<0.031	-	1.31	<b>105</b>
<b>TCPy</b>	2.5	<0.25	2.67	-	4.74	<b>83</b>	<0.25	3.09	-	5.73	<b>106</b>
<b>2,4,6-T</b>	2.5	<0.063	<0.063	-	2.84	<b>113</b>	<0.063	<0.063	-	3.11	<b>124</b>
<b>DCCA</b>	25	n.r.	n.r.	-	n.r.	-	n.r.	n.r.	-	n.r.	-
<b>Fluazifop (free acid)</b>	1.25	0.05	0.05	<b>-1</b>	1.01	<b>77</b>	0.03	0.05	<b>29</b>	1.12	<b>86</b>
<b>3PBA</b>	5	<0.13	0.99	-	6.56	<b>112</b>	<0.13	0.59	-	6.09	<b>110</b>
<b>4F3PBA</b>	2.5	<0.063	<0.063	-	2.43	<b>97</b>	<0.063	<0.063	-	2.52	<b>101</b>
<b>Quizalofop (free acid)</b>	1.25	<0.031	<0.031	-	1.30	<b>104</b>	<0.031	<0.031	-	1.29	<b>103</b>

<sup>a</sup> Compounds listed in order of retention times; EH, enzymatic hydrolysis; n.r., not reported.

**Table S6**

Study of the impact of thawing/freezing cycles on the conservation of the target substances: experiments on two urine pools (pools #1 and #3) spiked at an intermediate level.

Compound <sup>a</sup>	Pool #1							Pool #3								
	T <sub>0</sub>		1st cycle		2nd cycle		3rd cycle		T <sub>0</sub>		1st cycle		2nd cycle		3rd cycle	
	C (µg.L <sup>-1</sup> ) (RSD %)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	C (µg.L <sup>-1</sup> ) (RSD %)	ΔC (%)	
<b>Method n°1 (ESI-)</b>																
DMP	10.6 (26)	9.25 (17)	<b>-13%</b>	12.33 (21)	<b>16%</b>	9.62 (25)	<b>-10%</b>	8.78 (16)	9.09 (14)	<b>3%</b>	9.91 (17)	<b>13%</b>	9.54 (8)	<b>9%</b>		
DMTP	13.7 (14)	13.4 (16)	<b>-2%</b>	13.2 (6)	<b>-4%</b>	13.8 (16)	<b>1%</b>	11.5 (10)	10.9 (7)	<b>-5%</b>	10.4 (12)	<b>-9%</b>	10.3 (4)	<b>-10%</b>		
DEP	42.1 (23)	44.6 (9)	<b>6%</b>	45.1 (16)	<b>7%</b>	49.3 (13)	<b>17%</b>	11.8 (10)	13.4 (4)	<b>14%</b>	14.1 (8)	<b>20%</b>	12.6 (12)	<b>6%</b>		
DMDTP	3.91 (1)	3.93 (2)	<b>0%</b>	3.85 (7)	<b>-2%</b>	3.99 (6)	<b>2%</b>	3.77 (5)	3.79 (5)	<b>1%</b>	3.77 (2)	<b>0%</b>	3.49 (2)	<b>-7%</b>		
DETP	11.4 (1)	11.4 (6)	<b>-1%</b>	10.7 (2)	<b>-6%</b>	10.9 (7)	<b>-5%</b>	2.05 (5)	2.03 (2)	<b>-1%</b>	2.29 (19)	<b>11%</b>	2.09 (9)	<b>2%</b>		
2-(4-Hydroxyphenoxy)propanoic acid	1.95 (4)	1.81 (8)	<b>-8%</b>	1.65 (3)	<b>-15%</b>	1.79 (9)	<b>-8%</b>	1.29 (4)	1.30 (6)	<b>1%</b>	1.31 (4)	<b>2%</b>	1.33 (10)	<b>3%</b>		
6-Chloronicotinic acid	2.25 (6)	2.10 (5)	<b>-6%</b>	2.06 (5)	<b>-9%</b>	2.12 (4)	<b>-6%</b>	2.13 (0)	2.03 (5)	<b>-4%</b>	2.03 (1)	<b>-5%</b>	2.08 (6)	<b>-2%</b>		
Bromoxynil	0.455 (6)	0.478 (5)	<b>5%</b>	0.471 (6)	<b>4%</b>	0.484 (4)	<b>6%</b>	0.488 (13)	0.491 (5)	<b>1%</b>	0.470 (4)	<b>-4%</b>	0.462 (3)	<b>-5%</b>		
TCPy	2.27 (7)	2.31 (6)	<b>2%</b>	2.29 (4)	<b>1%</b>	2.41 (9)	<b>6%</b>	2.41 (7)	2.30 (1)	<b>-4%</b>	2.99 (19)	<b>24%</b>	2.95 (20)	<b>22%</b>		
2,4,6-T	1.36 (21)	1.29 (22)	<b>-5%</b>	1.56 (21)	<b>15%</b>	1.64 (5)	<b>21%</b>	0.92 (26)	1.05 (12)	<b>14%</b>	1.19 (3)	<b>30%</b>	1.17 (29)	<b>27%</b>		
DCCA	9.15 (5)	10.6 (4)	<b>16%</b>	10.6 (1)	<b>16%</b>	9.88 (9)	<b>8%</b>	10.2 (11)	9.99 (1)	<b>-2%</b>	10.0 (7)	<b>-2%</b>	9.79 (3)	<b>-4%</b>		
Fluazifop (free acid)	0.379 (2)	0.373 (5)	<b>-2%</b>	0.329 (9)	<b>-13%</b>	0.350 (3)	<b>-8%</b>	0.568 (8)	0.580 (7)	<b>2%</b>	0.555 (7)	<b>-2%</b>	0.533 (4)	<b>-6%</b>		
3PBA	2.04 (10)	2.08 (11)	<b>2%</b>	2.02 (9)	<b>-1%</b>	1.89 (4)	<b>-7%</b>	1.86 (10)	1.96 (13)	<b>5%</b>	1.81 (9)	<b>-2%</b>	1.88 (13)	<b>2%</b>		
4F3PBA	1.04 (7)	1.02 (2)	<b>-2%</b>	1.00 (4)	<b>-4%</b>	1.02 (3)	<b>-1%</b>	1.13 (6)	1.06 (7)	<b>-7%</b>	1.01 (9)	<b>-10%</b>	0.937 (10)	<b>-17%</b>		
Quizalofop (free acid)	0.517 (4)	0.485 (8)	<b>-6%</b>	0.468 (11)	<b>-10%</b>	0.469 (11)	<b>-9%</b>	0.522 (12)	0.482 (2)	<b>-8%</b>	0.494 (4)	<b>-6%</b>	0.426 (4)	<b>-19%</b>		
<b>Method n°2 (ESI+)</b>																
Nicotine	15.1 (3)	15.7 (3)	<b>4%</b>	15.0 (1)	<b>-1%</b>	15.5 (5)	<b>3%</b>	180 (3)	188 (2)	<b>5%</b>	202 (1)	<b>13%</b>	188 (2)	<b>5%</b>		
ADHP	4.08 (5)	3.25 (6)	<b>-20%</b>	2.65 (10)	<b>-35%</b>	3.28 (7)	<b>-20%</b>	1.76 (11)	1.98 (11)	<b>13%</b>	1.93 (13)	<b>10%</b>	1.79 (7)	<b>2%</b>		
Cotinine	7.46 (1)	7.69 (5)	<b>3%</b>	7.35 (3)	<b>-1%</b>	7.37 (2)	<b>-1%</b>	218 (3)	230 (4)	<b>6%</b>	243 (4)	<b>12%</b>	228 (4)	<b>5%</b>		

Carbendazim	0.752 (6)	0.733 (6)	-3%	0.720 (7)	-4%	0.800 (5)	6%	0.742 (4)	0.780 (14)	5%	0.785 (5)	6%	0.711 (10)	-4%
IMPy	1.81 (9)	1.78 (7)	-2%	1.81 (5)	0%	1.93 (4)	6%	1.37 (6)	1.32 (2)	-4%	1.35 (10)	-1%	1.36 (3)	0%
Dimethoate	0.766 (12)	0.761 (5)	-1%	0.742 (4)	-3%	0.740 (8)	-3%	0.711 (4)	0.719 (6)	1%	0.730 (7)	3%	0.693 (4)	-3%
3-Chloroaniline	3.76 (12)	4.55 (5)	21%	3.91 (12)	4%	3.52 (19)	-7%	3.64 (4)	2.90 (9)	-20%	3.10 (2)	-15%	3.05 (6)	-16%
Methyl-2-(2-hydroxyphenyl)-3-methylacrylate	31.3 (5)	30.4 (2)	-3%	28.4 (3)	-9%	28.7 (3)	-8%	59.7 (1)	60.9 (8)	2%	65.4 (5)	10%	60.7 (11)	2%
Dichlorvos	7.70 (4)	7.56 (8)	-2%	7.19 (7)	-7%	6.90 (10)	-10%	7.91 (4)	7.74 (1)	-2%	7.84 (6)	-1%	7.11 (2)	-10%
2-Methyl-6-ethylaniline	5.71 (3)	5.64 (10)	-1%	5.51 (5)	-3%	5.10 (4)	-11%	4.59 (9)	4.69 (3)	2%	4.80 (3)	5%	4.52 (2)	-2%
Carbofuran	0.858 (13)	0.881 (4)	3%	0.846 (13)	-1%	0.915 (7)	7%	1.32 (8)	1.31 (9)	0%	1.38 (5)	4%	1.38 (2)	4%
Carbofuran phenol	227 (12)	245 (5)	8%	246 (11)	8%	236 (7)	4%	311 (5)	317 (8)	2%	356 (12)	15%	339 (19)	9%
DCPU	2.81 (9)	3.00 (1)	7%	3.11 (9)	11%	2.90 (4)	3%	4.01 (11)	3.94 (18)	-2%	4.09 (6)	2%	4.47 (7)	12%
Fenpropimorph	1.57 (5)	1.39 (22)	-11%	1.55 (13)	-1%	1.27 (3)	-19%	2.73 (22)	2.32 (16)	-15%	2.67 (17)	-2%	2.32 (9)	-15%
IPPMU	1.45 (5)	1.55 (8)	6%	1.49 (10)	3%	1.50 (3)	3%	1.75 (6)	1.77 (4)	1%	2.02 (3)	15%	1.95 (7)	11%
DCPMU	1.43 (6)	1.36 (12)	-5%	1.26 (17)	-12%	1.35 (13)	-6%	1.56 (10)	1.49 (13)	-5%	1.62 (15)	4%	1.70 (23)	9%
Isoproturon	1.78 (8)	1.79 (8)	0%	1.66 (17)	-7%	1.62 (7)	-9%	1.73 (10)	1.70 (6)	-2%	1.93 (5)	11%	1.85 (9)	7%
3,5-Dichloroaniline	9.40 (5)	11.8 (11)	26%	10.9 (27)	16%	10.8 (18)	15%	4.71 (6)	4.25 (6)	-10%	4.32 (7)	-8%	4.36 (16)	-7%
2-Phenylphenol	304 (13)	348 (14)	15%	350 (15)	15%	350 (10)	15%	441 (12)	417 (2)	-5%	462 (18)	5%	436 (8)	-1%
Azoxystrobin	0.318 (11)	0.279 (8)	-12%	0.307 (5)	-3%	0.293 (9)	-8%	0.293 (14)	0.286 (7)	-2%	0.278 (6)	-5%	0.268 (2)	-8%
Chlorpropham	1.57 (6)	1.38 (9)	-12%	1.47 (25)	-6%	1.42 (2)	-10%	1.16 (9)	1.02 (10)	-13%	1.10 (6)	-5%	0.931 (27)	-20%
Malathion	0.301 (4)	0.281 (6)	-7%	0.324 (18)	8%	0.302 (12)	0%	0.292 (7)	0.285 (2)	-2%	0.250 (12)	-14%	0.248 (13)	-15%
Iprodione	1.59 (16)	1.59 (6)	0%	1.30 (10)	-18%	1.50 (9)	-6%	1.22 (5)	1.19 (13)	-2%	1.25 (10)	2%	1.25 (2)	3%
Acetochlor	0.778 (4)	0.704 (3)	-9%	0.788 (10)	1%	0.683 (16)	-12%	0.700 (9)	0.63 (15)	-10%	0.637 (8)	-9%	0.671 (5)	-4%
Phorate	1.46 (10)	1.25 (11)	-14%	1.15 (12)	-22%	0.908 (8)	-38%	1.40 (5)	1.18 (2)	-15%	1.14 (15)	-19%	0.816 (3)	-42%
Chlorpyrifos-methyl	1.28 (3)	1.20 (7)	-6%	1.14 (22)	-11%	1.11 (4)	-13%	1.35 (4)	1.10 (8)	-18%	0.872 (1)	-35%	0.821 (5)	-39%
Chlorpyrifos-ethyl	0.979 (31)	0.638 (26)	-35%	0.491 (7)	-50%	0.401 (30)	-59%	0.713 (23)	0.104 (91)	-85%	0.0427 (124)	-94%	0.0283 (173)	-96%

<sup>a</sup>Compounds listed in order of retention times

**Table S7**

Pesticide concentrations in fifteen human urine samples, method n°1 (ESI-).

Compound <sup>a</sup>	Measured concentrations ( $\mu\text{g.L}^{-1}$ )															n > LOD	Min	Max
	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Sample #8	Sample #9	Sample #10	Sample #11	Sample #12	Sample #13	Sample #14	Sample #15			
DMP	<0.63	8.6	38	8.0	36	<0.63	3.6	1.1	29	12	57	21	6.8	3.1	100	13	<0.63	100
DMTP	<0.63	8.0	30	7.0	42	<0.63	3.0	<0.63	28	14	41	25	7.9	2.4	65	12	<0.63	65
DEP	3.1	13	14	6.1	18	18	11	4.2	16	8.2	56	38	6.0	12	68	15	3.1	68
DMDTP	0.42	3.5	4.5	0.72	2.5	<0.25	0.86	0.30	11	3.8	2.9	1.3	4.1	0.42	20	14	<0.25	20
DETP	0.76	6.6	5.3	2.8	6.4	3.8	2.5	0.48	4.3	1.6	6.3	5.1	1.6	1.9	6.3	15	0.48	6.6
2-(4-Hydroxyphenoxy)propanoic acid	<0.25	<0.25	<0.25	0.33	1.4	<0.25	0.60	<0.25	<0.50	<0.50	<0.25	<0.25	<0.25	4.2	0.63	5	<0.25	4.2
6-Chloronicotinic acid	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.13	<0.25	<0.25	<0.13	<0.13	<0.13	<0.13	<0.13	0	<0.13	<0.25
Bromoxynil	<0.031	<0.031	0.055	0.057	0.034	<0.031	<0.031	<0.031	<0.063	<0.063	<0.031	<0.031	<0.031	<0.031	<0.031	3	<0.031	0.057
TCPy	1.0	0.27	0.67	2.6	8.1	1.3	0.92	1.9	12	3.1	3.4	1.5	0.84	0.64	14	15	0.27	14
2,4,6-T	<0.063	0.064	<0.063	0.084	0.079	<0.063	<0.063	<0.063	<0.13	0.21	<0.063	<0.063	<0.063	0.16	0.10	6	<0.063	0.21
DCCA	<0.63	<0.63	<0.63	13	<0.63	<0.63	<0.63	<0.63	<1.3	<1.3	<0.63	<0.63	0.95	3.0	7.3	4	<0.63	13
Fluazifop (free acid)	0.060	0.047	0.11	0.050	<0.031	<0.031	<0.031	0.066	0.20	<0.063	<0.031	0.054	<0.031	<0.031	0.17	8	<0.031	0.20
3PBA	0.26	0.24	0.40	5.4	1.6	0.28	0.43	<0.13	0.87	1.8	1.1	0.28	0.66	0.91	3.2	14	<0.13	5.4
4F3PBA	<0.063	<0.063	<0.063	0.083	<0.063	<0.063	<0.063	<0.063	<0.13	<0.13	<0.063	<0.063	<0.063	<0.063	<0.063	1	<0.063	0.083
Quizalofop (free acid)	0.037	<0.031	0.042	<0.031	<0.031	<0.031	<0.031	<0.031	0.18	<0.063	<0.031	<0.031	<0.031	<0.031	<0.031	3	<0.031	0.18

<sup>a</sup> Compounds listed in order of retention times

**Table S8**

Pesticide concentrations in fifteen human urine samples, method n°2 (ESI+).

Compound <sup>a</sup>	Measured concentrations ( $\mu\text{g.L}^{-1}$ )															n > LOD	Min	Max
	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6	Sample #7	Sample #8	Sample #9	Sample #10	Sample #11	Sample #12	Sample #13	Sample #14	Sample #15			
Nicotine	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<8.0	<8.0	<4.0	<4.0	<4.0	<4.0	<4.0	0	<4.0	<8.0	
ADHP	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<2.0	<2.0	<1.0	<1.0	<1.0	<1.0	<1.0	0	<1.0	<2.0	
Cotinine	<2.0	<2.0	9.6	<2.0	<2.0	<2.0	<2.0	4.5	<4.0	6.1	9.2	<2.0	<2.0	<2.0	4	<2.0	9.6	
Carbendazim	<0.050	<0.050	<0.050	<0.050	<0.050	0.16	0.11	<0.10	<0.10	<0.050	1.6	0.59	<0.050	<0.050	4	<0.050	1.6	
IMPy	<0.10	0.77	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	0.71	1.3	<0.10	<0.10	0.21	4	<0.10	1.3	
Dimethoate	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.10	<0.10	<0.050	<0.050	<0.050	<0.050	<0.050	0	<0.050	<0.10	
3-Chloroaniline	<0.25	<0.25	0.87	<0.25	<0.25	<0.25	<0.25	<0.50	<0.50	<0.25	<0.25	<0.25	<0.25	<0.25	1	<0.25	0.87	
Methyl-2-(2-hydroxyphenyl)-3-methylacrylate	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0	<16	<16	<8.0	<8.0	<8.0	<8.0	<8.0	0	<8.0	<16	
Dichlorvos	<0.50	<0.50	<0.50	<0.50	<5.0	<0.50	<0.50	<5.0	<1.0	<1.0	<0.50	<5.0	<0.50	<0.50	0	<0.50	<5.0	
2-Methyl-6-ethylaniline	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.50	<0.25	<0.25	<0.25	<0.25	<0.25	0	<0.25	<0.50	
Carbofuran	<0.20	<0.10	<0.10	<0.050	0.68	<0.050	<0.050	<0.050	<0.10	<0.10	<0.050	<0.050	<0.050	<0.050	1	<0.050	0.68	
Carbofuran phenol	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<8.0	<32	<4.0	<4.0	<4.0	<4.0	<4.0	0	<4.0	<32	
DCPU	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25	<0.50	<0.50	<0.25	<0.25	<0.25	<0.25	<0.25	0	<0.25	<0.50	
Fenpropimorph	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	<0.10	0	<0.10	<0.20	
IPPMU	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	<0.10	0	<0.10	<0.20	
DCPMU	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	<0.10	0	<0.10	<0.20	
Isoproturon	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	<0.10	0	<0.10	<0.20	
3,5-Dichloroaniline	1.4	0.53	3.8	<0.50	0.84	<0.50	0.64	0.57	<1.0	2.3	0.59	0.83	2.0	<0.50	2.3	II	<0.50	3.8
2-Phenylphenol	<25	<25	<25	<25	<25	<25	<25	<25	140	<50	<25	<25	<25	<25	1	<25	140	
Azoxystrobin	0.24	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.040	<0.040	<0.020	<0.020	<0.020	<0.020	1	<0.020	0.24	
Chlorpropham	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.40	<0.40	<0.20	<0.20	<0.20	<0.20	<0.20	0	<0.20	<0.40	
Malathion	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.040	<0.040	<0.020	<0.020	<0.020	<0.020	<0.020	0	<0.020	<0.040	
Iprodione	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	0	<0.10	<0.20	
Acetochlor	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.050	<0.10	<0.10	<0.050	<0.050	<0.050	<0.050	0	<0.050	<0.10	
Phorate	<0.10	<0.10	<0.10	<0.10	<0.10	0.13	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	1	<0.10	0.13	
Chlorpyrifos-methyl	<0.10	<0.10	<0.10	<0.10	<0.10	0.48	<0.10	<0.10	<0.20	<0.20	<0.10	<0.10	<0.10	<0.10	1	<0.10	0.48	
Chlorpyrifos-ethyl	<0.10	<0.10	<0.10	<0.10	<0.10	0.78	<0.10	<0.10	<0.20	0.54	<0.10	<0.10	<0.10	<0.10	2	<0.10	0.78	

<sup>a</sup> Compounds listed in order of retention times