

Supplementary Information

Pesticide Determination in Water Samples from a Rural Area by Multi-Target Method Applying Liquid Chromatography-Tandem Mass Spectrometry

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Table S1. UTM coordinates from the sampling points

Sampling point	UTM coordinate
SP 1	22k; 0455828; 7400659; elev 792 m
SP 2	22k; 0455759; 7401017; elev 769 m
SP 3	22k; 0455623; 7401677; elev 753 m
SP 4	22k; 0455844; 7401849; elev 786 m
SP 5	22k; 0458133; 7401759; elev 755 m
SP 6	22k; 0458494; 7401044; elev 786 m
SP 7	22k; 0457348; 7400402; elev 804 m
SP 8	22k; 0456752; 7401541; elev 845 m
SP 9	22k; 0456752; 7401541; elev 845 m

UTM: universal transverse Mercator conformal projection; elev: elevation or altitude.

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Table S2. Validation parameters of the quantitation method of pesticides in water samples

Pesticide	Slope	Intercept	R ²	Linear range / ($\mu\text{g L}^{-1}$) (n = 9)	LOD / ($\mu\text{g L}^{-1}$)	LOQ / ($\mu\text{g L}^{-1}$)	Accuracy			Precision		
							Recovery / % (n = 3)			RSD / % (n = 6)		
							0.25 $\mu\text{g L}^{-1}$	1.00 $\mu\text{g L}^{-1}$	50.00 $\mu\text{g L}^{-1}$	0.01 $\mu\text{g L}^{-1}$	1.00 $\mu\text{g L}^{-1}$	10.00 $\mu\text{g L}^{-1}$
Carbendazim	1297.10	-575.42	0.9741	0.01 to 50.00	0.003	0.010	55.58	86.84	92.79	1.37	4.88	4.48
Imidacloprid	53.53	-83.78	0.9995	0.01 to 50.00	0.003	0.010	94.05	115.67	103.84	5.97	13.62	5.24
Imazethapyr	155.22	-219.22	0.9978	0.05 to 50.00	0.010	0.050	112.91	110.06	98.03	7.60	8.32	3.19
Hexazinone	1905.40	1827.20	0.9998	0.01 to 50.00	0.003	0.010	108.08	80.46	91.72	1.96	18.62	5.03
Ametryn	4445.30	16895.00	0.9942	0.01 to 50.00	0.003	0.010	103.67	107.92	99.50	10.10	4.33	3.16
Atrazine	2390.30	6234.80	0.9974	0.01 to 50.00	0.003	0.010	112.87	91.88	97.68	2.08	4.74	3.65
Imazaquin	352.19	305.24	0.9980	0.01 to 50.00	0.003	0.010	77.03	98.58	91.04	4.96	11.49	6.75
Tebuthiuron	2284.80	6812.10	0.9927	0.01 to 50.00	0.003	0.010	106.31	73.98	89.56	10.89	11.26	4.80
Diuron	174.89	-434.96	0.9985	0.01 to 50.00	0.003	0.010	88.25	106.74	94.83	14.53	10.66	6.30
Azoxystrobin	1009.30	-1141.00	0.9981	0.10 to 50.00	0.010	0.100	97.36	102.49	109.83	2.92	13.57	2.79
Propiconazole	2039.10	-335.29	0.9926	0.01 to 50.00	0.003	0.010	103.60	92.59	106.38	7.74	3.44	4.74
Tebuconazole	1585.70	-8867.70	0.9920	0.01 to 50.00	0.003	0.010	103.86	108.43	103.78	8.04	8.63	9.32

R²: coefficient of determination; LOD: limit of detection; LOQ: limit of quantitation; RSD: relative standard deviation.

Table S3. Pesticide concentrations in water bodies quantified by LC-MS/MS in different sampling points collected in March

Pesticide	Sampling points, mean \pm SD / ($\mu\text{g L}^{-1}$) (n = 3)								
	1	2	3	4	5	6	7	8	9
Carbendazim	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00				0.01 \pm 0.00
Imidacloprid	0.01 \pm 0.00	0.01 \pm 0.00		0.01 \pm 0.00	0.03 \pm 0.00		0.01 \pm 0.00	0.01 \pm 0.00	0.05 \pm 0.01
Imazethapyr		< LOQ	< LOQ	0.31 \pm 0.05	6.18 \pm 0.91	< LOQ	3.850 \pm 0.55		< LOQ
Hexazinone									
Ametryn	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.05 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Atrazine	0.02 \pm 0.00	0.02 \pm 0.00	0.02 \pm 0.00	0.08 \pm 0.01	0.18 \pm 0.02	0.01 \pm 0.00	0.50 \pm 0.04	0.02 \pm 0.00	0.90 \pm 0.04
Imazaquin	0.01 \pm 0.00	0.04 \pm 0.00	0.02 \pm 0.00	0.16 \pm 0.03	0.50 \pm 0.06	0.01 \pm 0.00	0.57 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Tebuthiuron				0.18 \pm 0.02	0.08 \pm 0.01		0.01 \pm 0.07		0.01 \pm 0.00
Diuron	0.16 \pm 0.01	0.26 \pm 0.04	0.18 \pm 0.03	0.29 \pm 0.03	5.29 \pm 0.46	0.16 \pm 0.00	6.25 \pm 0.85	0.16 \pm 0.00	1.03 \pm 0.19
Azoxystrobin									
Propiconazole	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.11 \pm 0.01	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Tebuconazole	0.06 \pm 0.00	0.07 \pm 0.01	0.06 \pm 0.00	0.56 \pm 0.10	0.13 \pm 0.01	0.06 \pm 0.00	0.06 \pm 0.00	0.06 \pm 0.00	0.11 \pm 0.01
Total	0.29 \pm 0.02	0.44 \pm 0.06	0.31 \pm 0.03	1.62 \pm 0.24	12.54 \pm 1.49	0.28 \pm 0.01	11.26 \pm 1.51	0.28 \pm 0.00	2.14 \pm 0.26

LC-MS/MS: liquid chromatography-tandem mass spectrometry; SD: standard deviation; LOQ: limit of quantitation; < LOQ: values are lower than limit of quantitation.

Table S4. Pesticides concentration in water bodies quantified by LC-MS/MS in different sampling points collected in June

Pesticide	Sampling points, mean \pm SD / ($\mu\text{g L}^{-1}$) (n = 3)								
	1	2	3	4	5	6	7	8	9
Carbendazim	0.16 \pm 0.01	0.43 \pm 0.03	0.08 \pm 0.01	0.11 \pm 0.01	0.22 \pm 0.02	0.01 \pm 0.00	0.49 \pm 0.04	0.01 \pm 0.00	0.22 \pm 0.03
Imidacloprid		0.01 \pm 0.00		0.01 \pm 0.00	0.06 \pm 0.01				0.07 \pm 0.01
Imazethapyr		< LOQ		0.13 \pm 0.00	5.34 \pm 0.54		6.54 \pm 0.72	< LOQ	< LOQ
Hexazinone				0.03 \pm 0.00	0.14 \pm 0.02				0.04 \pm 0.01
Ametryn	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.04 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Atrazine	0.03 \pm 0.00	0.02 \pm 0.00	0.02 \pm 0.00	0.07 \pm 0.00	0.13 \pm 0.01	0.01 \pm 0.00	0.58 \pm 0.02	0.02 \pm 0.00	1.02 \pm 0.14
Imazaquin	0.01 \pm 0.00	0.05 \pm 0.01	0.03 \pm 0.01	0.13 \pm 0.02	0.63 \pm 0.11	0.01 \pm 0.00	0.96 \pm 0.15	0.01 \pm 0.00	0.01 \pm 0.00
Tebuthiuron			0.01 \pm 0.00	0.16 \pm 0.02	0.08 \pm 0.01		0.01 \pm 0.00		0.01 \pm 0.00
Diuron	0.17 \pm 0.02	0.39 \pm 0.06	0.20 \pm 0.04	0.27 \pm 0.04	6.05 \pm 0.22	0.16 \pm 0.01	10.63 \pm 0.04	0.17 \pm 0.01	1.22 \pm 0.21
Azoxystrobin									
Propiconazole	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.15 \pm 0.02	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Tebuconazole	0.06 \pm 0.00	0.09 \pm 0.01	0.06 \pm 0.00	0.66 \pm 0.12	0.12 \pm 0.02	0.05 \pm 0.00	0.06 \pm 0.00	0.06 \pm 0.00	0.10 \pm 0.02
Total	0.45 \pm 0.04	1.04 \pm 0.12	0.41 \pm 0.05	1.59 \pm 0.23	12.95 \pm 0.98	0.28 \pm 0.02	19.29 \pm 0.98	0.31 \pm 0.02	2.72 \pm 0.43

LC-MS/MS: liquid chromatography-tandem mass spectrometry; SD: standard deviation; LOQ: limit of quantitation; < LOQ: values are lower than limit of quantitation.

Table S5. Pesticides concentration in water bodies quantified by LC-MS/MS in different sampling points collected in September

Pesticide	Sampling points, mean \pm SD / ($\mu\text{g L}^{-1}$) (n = 3)								
	1	2	3	4	5	6	7	8	9
Carbendazim	0.15 \pm 0.01	0.07 \pm 0.01	0.05 \pm 0.01	0.06 \pm 0.01	0.04 \pm 0.01	0.02 \pm 0.00	0.05 \pm 0.01		0.17 \pm 0.02
Imidacloprid	0.01 \pm 0.00	0.01 \pm 0.00	0.00 \pm 0.00	0.02 \pm 0.00	0.05 \pm 0.02	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.10 \pm 0.01
Imazethapyr		0.05 \pm 0.01	< LOQ	0.07 \pm 0.01	1.77 \pm 0.33	0.14 \pm 0.00	4.28 \pm 0.47	< LOQ	< LOQ
Hexazinone	0.01 \pm 0.00			0.03 \pm 0.00	0.07 \pm 0.01				0.05 \pm 0.00
Ametryn	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Atrazine	0.03 \pm 0.00	0.03 \pm 0.00	0.03 \pm 0.00	0.08 \pm 0.00	0.11 \pm 0.01	0.03 \pm 0.00	0.59 \pm 0.02	0.03 \pm 0.00	1.02 \pm 0.04
Imazaquin	0.01 \pm 0.00	0.03 \pm 0.00	0.02 \pm 0.00	0.05 \pm 0.01	0.14 \pm 0.03	0.01 \pm 0.00	0.36 \pm 0.07	0.01 \pm 0.00	0.01 \pm 0.00
Tebuthiuron				0.18 \pm 0.02	0.06 \pm 0.01		0.01 \pm 0.00		0.01 \pm 0.00
Diuron	0.21 \pm 0.02	0.36 \pm 0.00	0.20 \pm 0.03	0.26 \pm 0.05	3.80 \pm 0.42	0.16 \pm 0.00	10.33 \pm 0.28	0.17 \pm 0.02	1.04 \pm 0.18
Azoxystrobin						< LOQ		< LOQ	
Propiconazole	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.16 \pm 0.03	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Tebuconazole	0.06 \pm 0.01	0.07 \pm 0.05	0.06 \pm 0.00	0.80 \pm 0.13	0.11 \pm 0.01	0.06 \pm 0.00	0.06 \pm 0.00	0.06 \pm 0.00	0.10 \pm 0.01
Total	0.50 \pm 0.05	0.64 \pm 0.05	0.40 \pm 0.04	1.57 \pm 0.24	6.33 \pm 0.87	0.45 \pm 0.01	15.70 \pm 0.85	0.33 \pm 0.02	2.52 \pm 0.27

LC-MS/MS: liquid chromatography-tandem mass spectrometry; SD: standard deviation; LOQ: limit of quantitation; < LOQ: values are lower than limit of quantitation.

Table S6. Pesticide concentrations in water bodies quantified by LC-MS/MS in different sampling points collected in December

Pesticide	Sampling points, mean \pm SD / ($\mu\text{g L}^{-1}$) (n = 3)								
	1	2	3	4	5	6	7	8	9
Carbendazim	0.43 \pm 0.03	0.35 \pm 0.02	0.02 \pm 0.00	0.11 \pm 0.01	0.15 \pm 0.01	0.01 \pm 0.00	0.97 \pm 0.07		0.08 \pm 0.01
Imidacloprid	0.02 \pm 0.00		0.01 \pm 0.00	0.03 \pm 0.00	0.03 \pm 0.00	0.01 \pm 0.00		0.01 \pm 0.00	0.16 \pm 0.02
Imazethapyr		< LOQ		< LOQ	2.69 \pm 0.34		5.75 \pm 0.67		< LOQ
Hexazinone	0.09 \pm 0.02			0.03 \pm 0.00	0.11 \pm 0.02				0.11 \pm 0.02
Ametryn	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.03 \pm 0.00	0.01 \pm 0.00		0.01 \pm 0.00	0.01 \pm 0.00
Atrazine	0.04 \pm 0.00	0.02 \pm 0.00	0.03 \pm 0.00	0.05 \pm 0.00	0.11 \pm 0.00	0.02 \pm 0.00	0.57 \pm 0.04	0.02 \pm 0.00	1.40 \pm 0.07
Imazaquin	0.01 \pm 0.00	0.04 \pm 0.00	0.01 \pm 0.00	0.06 \pm 0.01	0.36 \pm 0.05	0.01 \pm 0.00	0.66 \pm 0.09	0.01 \pm 0.00	0.02 \pm 0.00
Tebuthiuron				0.11 \pm 0.01	0.09 \pm 0.01		0.01 \pm 0.00		0.02 \pm 0.00
Diuron	0.86 \pm 0.17	0.31 \pm 0.06	0.23 \pm 0.04	0.24 \pm 0.05	4.66 \pm 0.18	0.16 \pm 0.00	12.59 \pm 0.64	0.16 \pm 0.00	1.56 \pm 0.29
Azoxystrobin	< LOQ								
Propiconazole	0.01 \pm 0.00	0.02 \pm 0.00	0.01 \pm 0.00	0.02 \pm 0.00	0.19 \pm 0.03	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00	0.01 \pm 0.00
Tebuconazole	0.06 \pm 0.00	0.08 \pm 0.01	0.06 \pm 0.00	0.61 \pm 0.08	0.12 \pm 0.02	0.06 \pm 0.00	0.06 \pm 0.00	0.06 \pm 0.00	0.18 \pm 0.03
Total	1.55 \pm 0.23	0.85 \pm 0.00	0.38 \pm 0.05	1.30 \pm 0.16	8.52 \pm 0.66	0.28 \pm 0.01	20.63 \pm 1.61	0.28 \pm 0.01	3.55 \pm 0.44

LC-MS/MS: liquid chromatography-tandem mass spectrometry; SD: standard deviation; LOQ: limit of quantitation; < LOQ: values are lower than limit of quantitation.

