

Supplementary Material

SPE-LC-MS/MS analysis of chiral and achiral fungicides in drinking water

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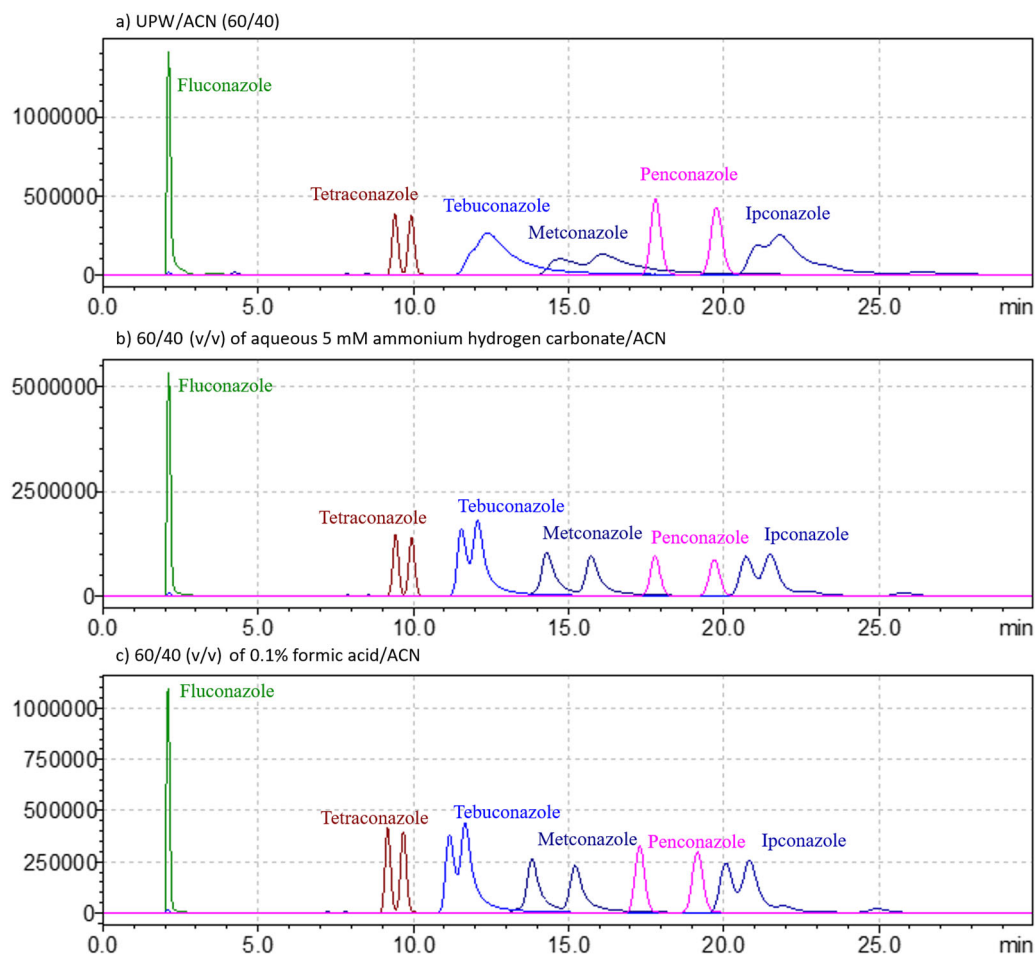


Figure S1. LC-MS/MS chromatograms of a solution of 10 mg L⁻¹ of each target analyte, obtained in a column Lux® 3 µm i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), using different mobile phases (60/40, v/v of UPW/ACN (a); 60/40 (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN (b); 60/40 (v/v) of 0.1% formic acid UPW/ACN (c)), the column oven temperature set at 45°C, a flow rate of 0.25 mL min⁻¹ and an injection volume of 10 µL. See details in Table S2.

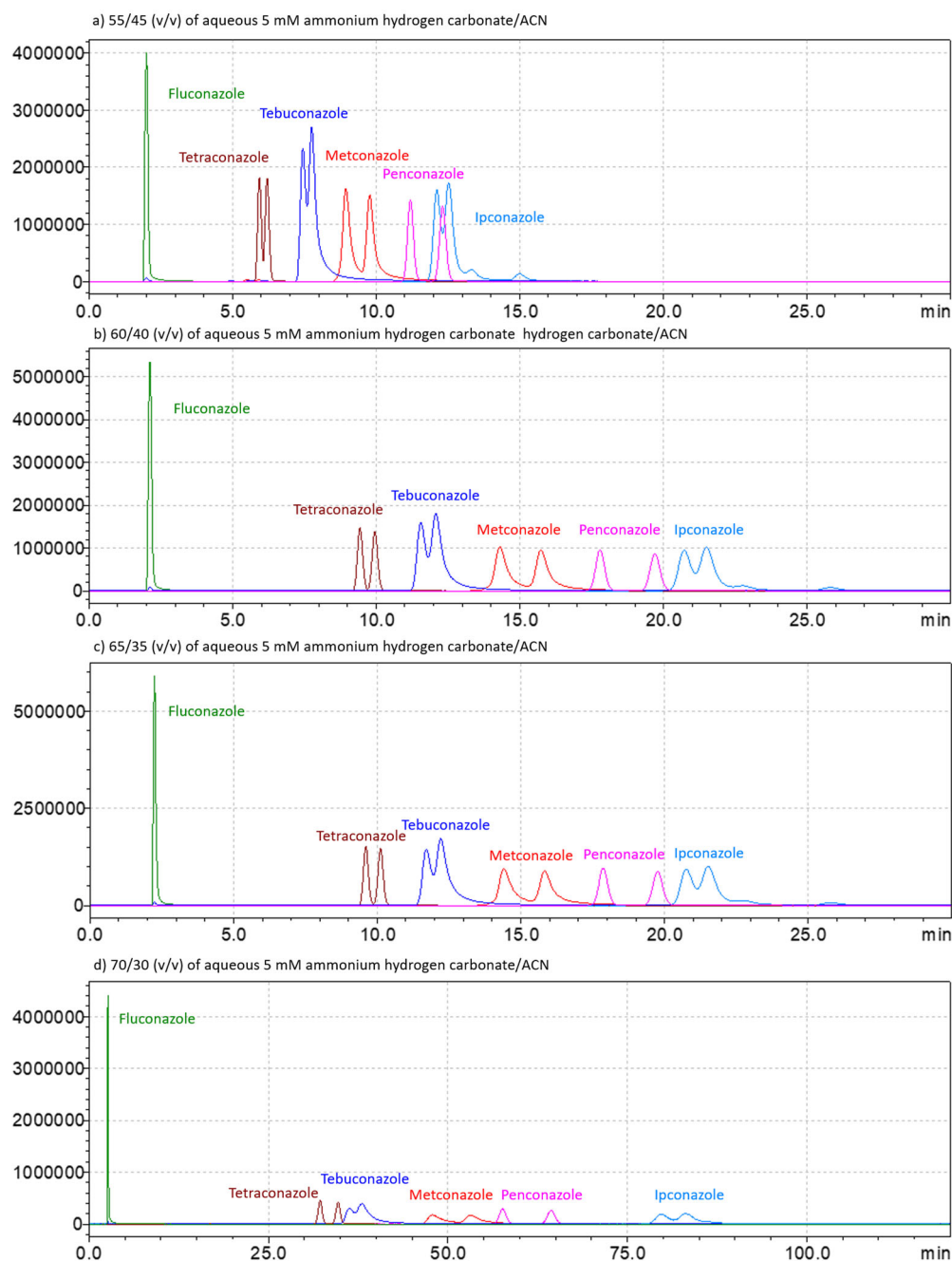


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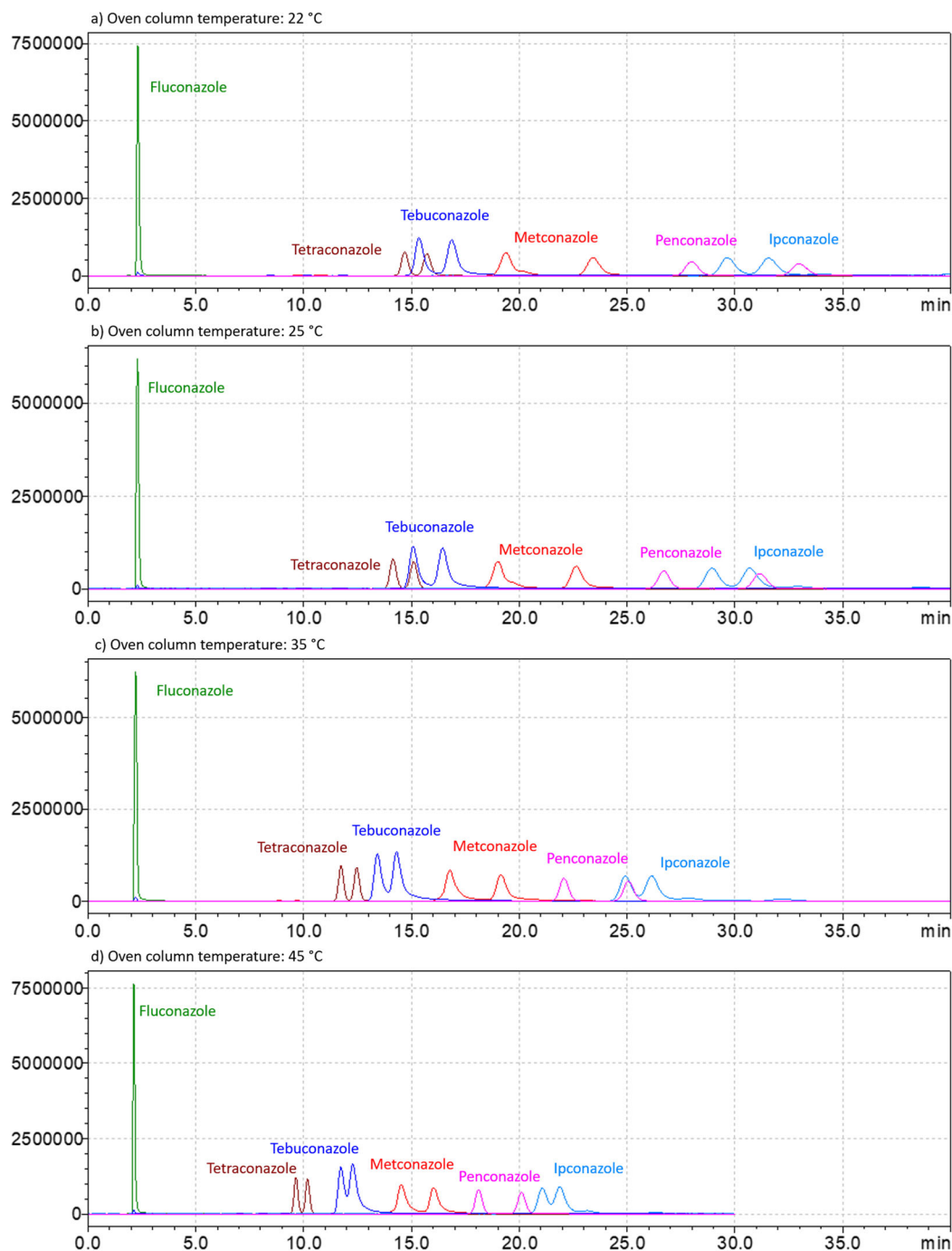


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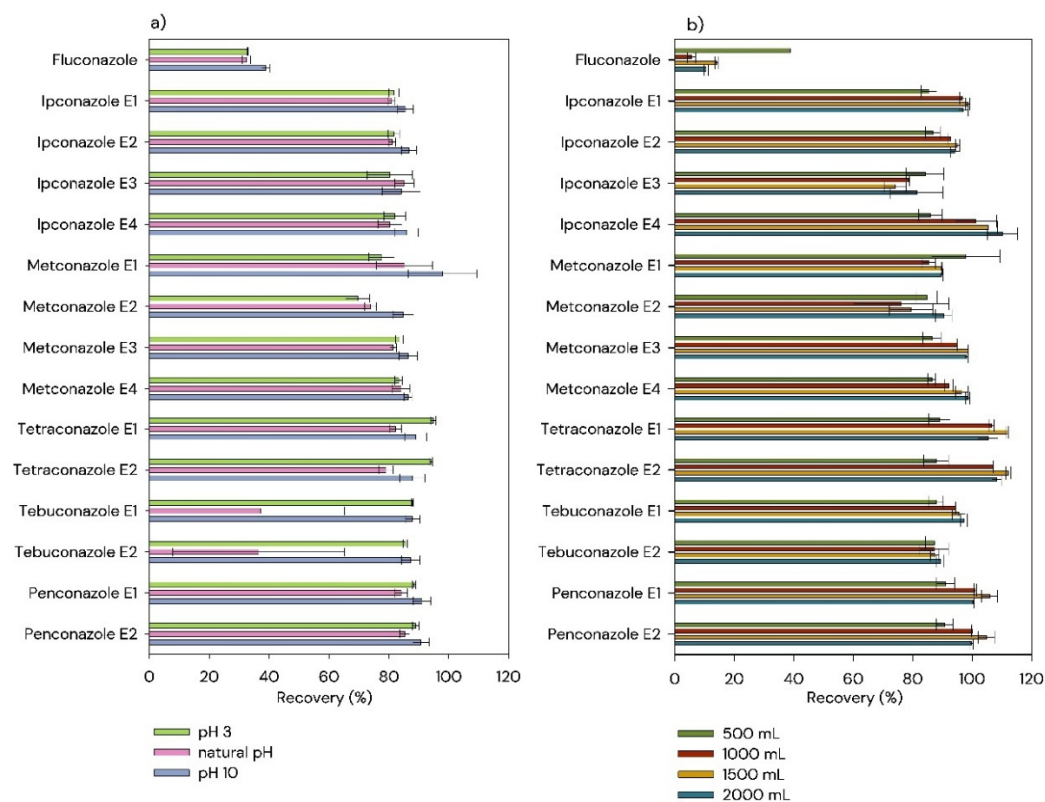


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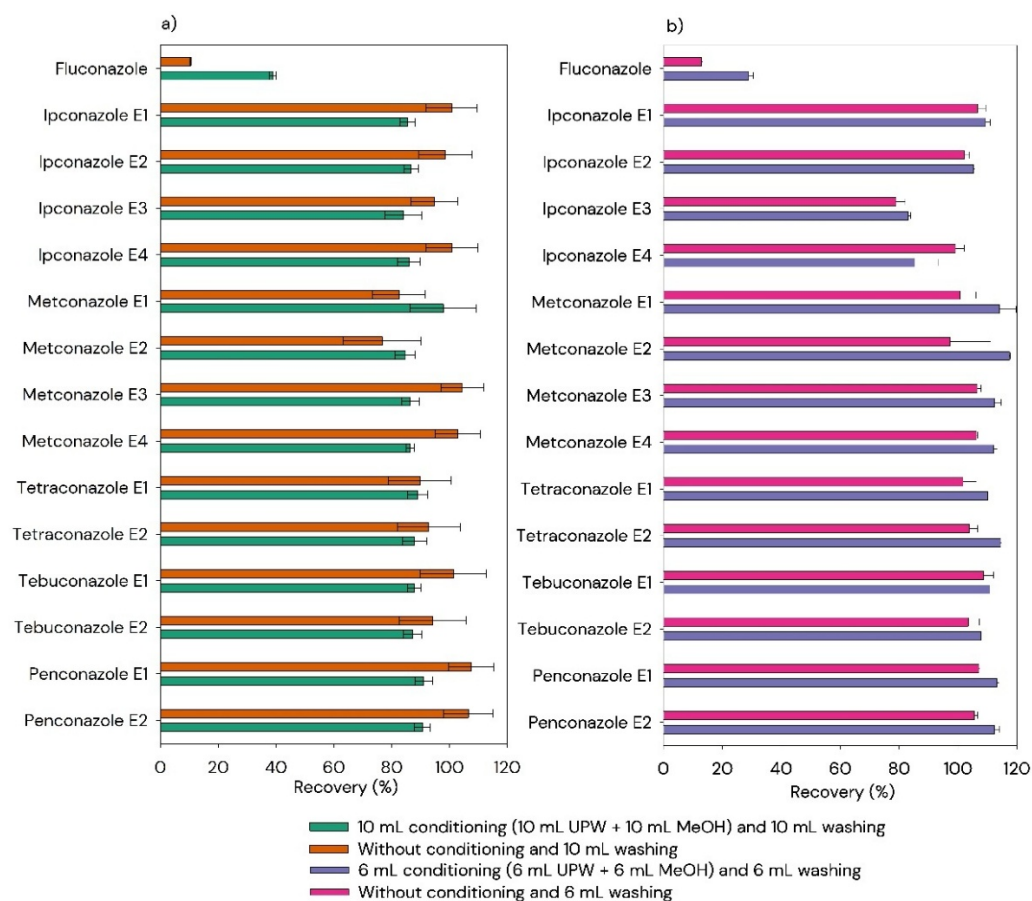


Figure S5. Recovery (%) of the target analytes from DW containing each at 100 ng L⁻¹, using different conditioning and washing volumes: with and without conditioning with 10 mL washing (a); with and without conditioning with 6 mL washing (b).

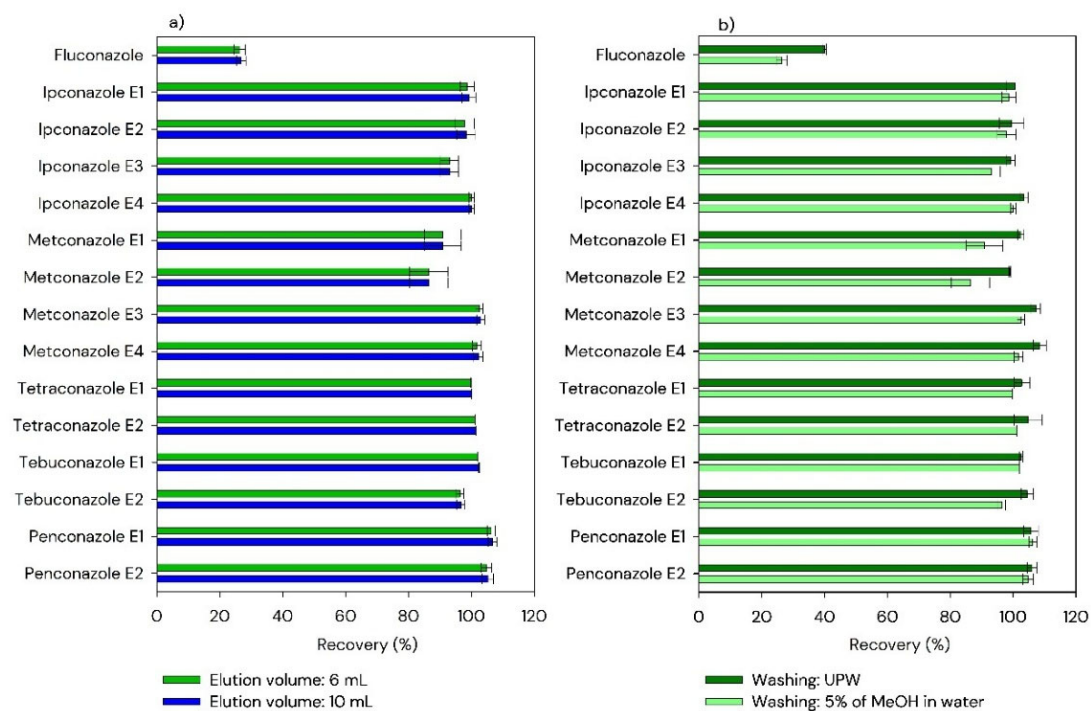


Figure S6. Recovery (%) of the target analytes from DW containing each at 100 ng L⁻¹, when using different elution volumes (6 mL or 10 mL) (a); using different washing solvents: UPW with 5% MeOH and UPW without 5% MeOH (b).

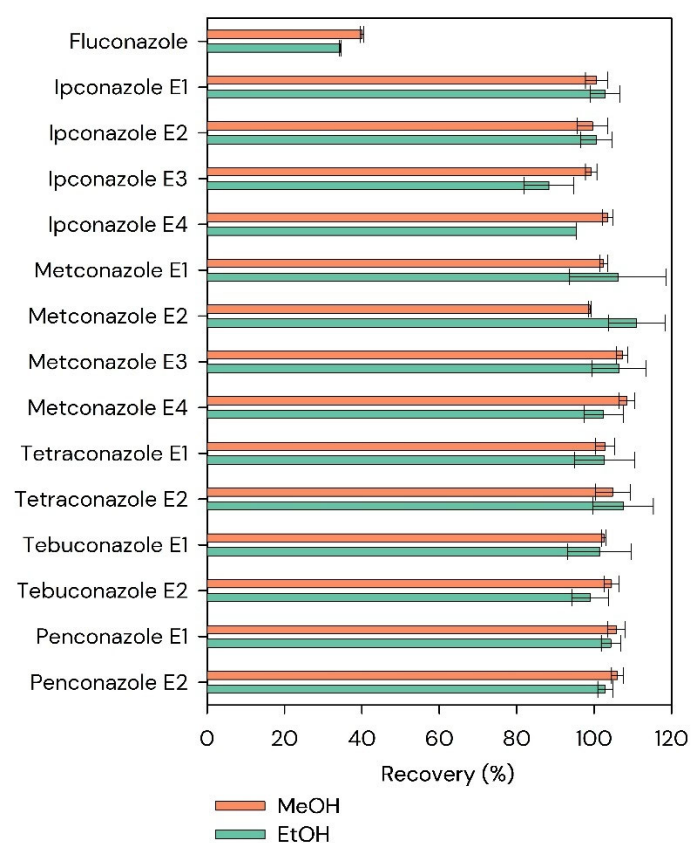


Figure S7. Recovery (%) of the target analytes from DW containing each at 100 ng L⁻¹, using MeOH in conditioning (10 mL UPW and 10 mL MeOH) and elution (6 mL MeOH) and with EtOH in conditioning (10 mL UPW and 10 mL EtOH) and elution (6 mL EtOH).

Table S1. Selected reaction monitoring (SRM) parameters for tandem mass spectrometry analysis of target analytes, after Electrospray Ionization under positive mode (DP is the declustering potential; CE is the collision energy; CXP is the collision cell exit potential).

Analyte	Precursor ion (m/z)	IS	Quantification (SRM1)				Confirmation (SRM2)				Confirmation (SRM3)				Ion ratio	
			Product ion	DP (V)	CE (V)	CXP (V)	Product ion	DP (V)	CE (V)	CXP (V)	Product ion	DP (V)	CE (V)	CXP (V)	SRM1/2	SRM1/3
Fluconazole-d ₄ (1)	311.00	-	223.05	-23	-19	-24	-	-	-	-	-	-	-	-	-	-
Penconazole-d ₇ E1 (2)	292.75	-	71.15	-15	-22	-27	-	-	-	-	-	-	-	-	-	-
Penconazole-d ₇ E2 (3)	292.75	-	71.15	-15	-22	-27	-	-	-	-	-	-	-	-	-	-
Fluconazole (1)	307.05	1	220.10	-15	-21	-22	238.10	-15	-17	-24	-	-	-	-	1.0	-
Ipconazole E1 (2)	334.10	2	70.05	-16	-21	-27	124.95	-16	-43	-23	-	-	-	-	7.4	-
Ipconazole E2 (3)	334.10	3	70.05	-16	-21	-27	124.95	-16	-43	-23	-	-	-	-	7.1	-
Ipconazole E3 (2)	334.10	2	70.05	-16	-21	-27	124.95	-16	-43	-23	-	-	-	-	5.8	-
Ipconazole E4 (3)	334.10	3	70.05	-16	-21	-27	124.95	-16	-43	-23	-	-	-	-	5.1	-
Metconazole E1 (2)	320.10	2	70.05	-15	-25	-26	124.9	-15	-45	-21	-	-	-	-	2.7	-
Metconazole E2 (3)	320.10	3	70.05	-15	-25	-26	124.9	-15	-45	-21	-	-	-	-	2.6	-
Metconazole E3 (2)	320.10	2	70.05	-15	-25	-26	124.9	-15	-45	-21	-	-	-	-	8.2	-
Metconazole E4 (3)	320.10	3	70.05	-15	-25	-26	124.9	-15	-45	-21	-	-	-	-	8.6	-
Penconazole E1 (2)	284.00	2	70.05	-28	-19	-26	158.95	-28	-25	-30	-	-	-	-	1.5	-
Penconazole E2 (3)	284.00	3	70.05	-28	-19	-26	158.95	-28	-25	-30	-	-	-	-	1.5	-
Tebuconazole E1 (2)	308.10	2	70.0	-15	-23	-28	124.90	-15	-35	-11	115.85	-15	-41	-10	10.9	41.0
Tebuconazole E2 (3)	308.10	3	70.0	-15	-23	-28	124.90	-15	-35	-11	115.85	-15	-41	-10	11.6	43.2
Tetraconazole E1 (2)	371.90	2	158.90	-17	-35	-29	70.05	-17	-24	-25	-	-	-	-	1.9	-
Tetraconazole E2 (3)	371.90	3	158.90	-17	-35	-29	70.05	-17	-24	-25	-	-	-	-	2.3	-

Table S2 Chromatographic parameters (retention time (t_R), min), capacity (k) and selectivity factors (α) and resolution (Rs)) obtained for the (enantio)separation of the target fungicides in a solution of 10 mg L⁻¹ of each, by LC-MS/MS on a Lux® 3 μ m i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), under the reverse-elution mode, using different mobile phases (60/40 (v/v) of UPW/ACN (a); 60/40 (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN (b); 60/40 (v/v) of UPW/ACN with 0.1% formic acid (c)), the column oven temperature set at 45°C, a flow rate of 0.25 mL min⁻¹ and an injection volume of 10 μ L.

		a (60/40 (v/v) of UPW/ACN)				b (60/40 (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN)				c (60/40 (v/v) of UPW/ACN with 0.1% formic acid)			
Fungicide		t_R	k	α	Rs	t_R	k	α	Rs	t_R	k	α	Rs
Fluconazole		2.12	0.88	-	-	2.12	0.88	-	-	2.10	0.86	-	-
Tetraconazole	E1	9.41	3.92	1.06	1.35	9.44	7.35	1.06	1.33	9.18	7.12	1.06	1.31
	E2	9.94	4.17			9.95	7.81			9.69	7.57		
Tebuconazole	E1	12.4	-	-	-	11.6	9.23	1.05	0.74	11.2	8.89	1.05	0.73
	E2	-	-			12.1	9.69			11.7	9.33		
Metconazole	E1	7.86	5.95	-	-	7.9	5.99	-	-	7.24	5.41	-	-
	E2	8.52	6.54	1.10	1.73	8.6	6.57	1.10	1.84	7.83	5.93	1.10	1.83
	E3	14.7	12.0	1.84	4.65	14.3	11.7	1.77	10.0	13.8	11.2	1.90	11.6
	E4	16.1	13.2	1.10	0.56	15.7	12.9	1.11	1.83	15.2	12.5	1.11	1.89
Penconazole	E1	17.8	14.8	1.12	2.95	17.8	14.7	1.12	2.96	17.3	14.3	1.12	2.94
	E2	19.8	16.5			19.7	16.4			19.2	16.0		
Ipconazole	E1	21.1	17.7	-	-	20.7	17.3	-	-	20.1	16.8	-	-
	E2	21.8	18.3	1.04	0.29	21.5	18.0	1.04	0.82	20.8	17.4	1.04	0.83
	E3	26.4	22.4	1.22	2.23	22.7	19.1	1.06	0.95	21.9	18.4	1.05	0.72
	E4	-	-	-	-	25.8	21.8	1.14	2.36	25.0	21.1	1.15	2.10

Table S3. Chromatographic parameters (retention time (t_R), min), capacity (k) and selectivity factors (α) and resolution (R_s)) obtained for the (enantio)separation of the target fungicides in a solution of 10 mg L⁻¹ of each, by LC-MS/MS on a Lux® 3 μ m i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), under the reverse-elution mode, using different proportions (v/v) of aqueous 5 mM ammonium hydrogen carbonate and ACN (v/v) the in mobile phase (55/45 (a); 60/40 (b); 65/45 (c); 70/30 (d)), the column oven temperature set at 45°C, a flow rate of 0.25 mL min⁻¹ and an injection volume of 10 μ L.

		a (55/45)				b (60/40)				c (65/35)				d (70/30)			
Fungicide		t_R	k	α	R_s	t_R	k	α	R_s	t_R	k	α	R_s	t_R	k	α	R_s
Fluconazole		2.00	0.77	-	-	2.12	0.88	-	-	2.30	1.04	-	-	2.61	1.31	-	-
Tetraconazole	E1	5.94	4.25	1.06	0.92	9.44	7.35	1.06	1.33	16.2	13.4	1.07	1.77	32.2	27.5	1.08	2.27
	E2	6.20	4.49			10.0	7.81			17.3	14.3			34.7	29.7		
Tebuconazole	E1	7.45	5.59	1.05	0.61	11.6	9.23	1.05	0.74	19.2	16.0	1.05	0.62	36.3	31.1	1.05	0.62
	E2	7.76	5.86			12.1	9.69			20.1	16.8			38.1	32.7		
Metconazole	E1	5.51	3.88	-	-	7.9	5.99	-	-	12.1	9.74	-	-	21.4	17.9	-	-
	E2	5.92	4.33	1.09	1.56	8.6	6.57	1.10	1.84	13.3	10.7	1.10	2.50	23.5	19.8	1.10	2.45
	E3	8.94	6.92	1.63	7.78	14.3	11.7	1.77	10.0	24.5	20.7	1.93	11.2	47.9	41.4	2.10	10.9
	E4	9.78	7.65	1.11	1.63	15.7	12.93	1.11	1.83	27.1	20.0	1.11	1.68	53.1	46.0	1.11	1.37
Penconazole	E1	11.2	8.91	1.11	2.56	17.8	14.7	1.12	2.96	30.1	25.6	1.12	3.25	57.6	50.0	1.12	3.46
	E2	12.3	9.90			19.7	16.4			33.5	28.6			64.4	56.0		
Ipconazole	E1	12.1	9.72	-	-	20.7	17.3	-	-	38.0	32.6	-	-	79.9	69.7	-	-
	E2	12.5	10.1	1.04	0.67	21.5	18.0	1.04	0.82	39.5	34.0	1.04	0.84	83.1	72.5	1.04	0.83
	E3	13.3	10.8	1.07	1.02	22.7	19.1	1.06	0.95	40.6	35.6	1.05	0.60	99.7	87.2	1.20	3.94
	E4	15.0	12.3	1.14	2.26	25.8	21.8	1.14	2.36	47.4	41.0	1.15	2.01	-	-	-	-

Table S4. Chromatographic parameters (retention time (t_R), min), capacity (k) and selectivity factors (α) and resolution (Rs)) obtained for the (enantio)separation of the target fungicides in a solution of 10 mg L⁻¹ of each, by LC-MS/MS on a Lux® 3 μ m i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), under the reverse-elution mode, using a mobile phase composed of 60/40 (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN, a flow rate of 0.25 mL min⁻¹, an injection volume of 10 μ L, and the following oven column temperatures: 22°C (a); 25 °C (b); 35 °C (c), and 45 °C (d).

		a (22 °C)				b (25 °C)				c (35 °C)				d (45 °C)			
Fungicide		t_R / min	k	α	Rs	t_R /min	k	α	Rs	t_R /min	k	α	Rs	t_R /min	k	α	Rs
Fluconazole		2.32	1.05	-	-	2.30	1.03	-	-	2.21	0.95	-	-	2.1	0.88	-	-
Tetraconazole	E1	14.6	12.0	1.08	1.58	14.1	11.5	1.07	1.59	11.7	11.5	1.07	1.59	9.4	7.35	1.06	1.33
	E2	15.7	12.9			15.1	12.4			12.5	12.4			10.0	7.81		
Tebuconazole	E1	15.3	12.5	1.11	1.88	15.1	12.3	1.10	1.74	13.4	10.9	1.07	1.24	11.6	9.23	1.05	0.74
	E2	16.8	13.9			16.5	13.6			14.3	11.7			12.1	9.69		
Metconazole	E1	9.72	7.60	-	-	9.60	7.52	-	-	8.85	6.83	-	-	7.90	5.99	-	-
	E2	10.7	8.54	1.12	1.94	10.7	8.43	1.12	1.92	9.70	7.58	1.11	2.09	8.56	6.57	1.10	1.84
	E3	19.3	16.1	1.89	11.1	19.0	15.8	1.88	11.3	16.8	13.8	1.82	11.2	14.3	11.7	1.77	10.0
	E4	23.4	19.7	1.22	3.83	22.6	19.0	1.20	3.78	19.2	16.0	1.15	2.74	15.7	12.9	1.11	1.83
Penconazole	E1	27.9	23.7	1.19	3.83	26.7	22.7	1.18	3.94	22.1	18.5	1.14	3.45	17.8	14.7	1.12	2.96
	E2	32.9	28.1			31.2	26.6			25.1	21.2			19.7	16.4		
Ipconazole	E1	29.6	25.2	-	-	29.0	24.6	-	-	24.9	21.1	-	-	20.7	17.3	-	-
	E2	31.5	26.9	1.07	1.39	30.7	26.2	1.06	1.32	26.1	22.1	1.05	1.13	21.5	18.0	1.04	0.82
	E3	33.8	28.9	1.08	1.43	32.9	28.1	1.08	1.28	27.8	23.6	1.07	1.27	22.7	19.1	1.06	0.95
	E4	39.9	34.3	1.19	3.55	38.6	33.2	1.18	3.04	32.2	27.5	1.16	3.28	25.8	21.8	1.14	2.36

Table S5. Chromatographic parameters (retention time (t_R), min), capacity (k) and selectivity factors (α) and resolution (Rs)) obtained for the (enantio)separation of the target fungicides in a solution of 10 mg L⁻¹ of each, by LC-MS/MS on a Lux[®] 3 μ m i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), under the reverse-elution mode, using different proportions (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN (55/45 (a); 60/40 (b); 65/45 (c)), the column oven temperature set at 25°C, a flow rate of 0.25 mL min⁻¹ and an injection volume of 10 μ L.

		a (55/45)				b (60/40)				c (65/35)			
Fungicide		t_R	k	α	Rs	t_R	k	α	Rs	t_R	k	α	Rs
Fluconazole		2.13	0.88	-	-	2.29	1.02	-	-	2.57	1.27	-	-
Tetraconazole	E1	8.13	6.20	1.07	1.17	13.9	11.5	1.07	1.59	27.5	23.3	1.08	1.97
	E2	8.61	6.62			14.8	12.4			29.5	25.2		
Tebuconazole	E1	9.33	7.17	1.10	1.54	14.8	12.1	1.10	1.72	27.0	22.9	1.10	1.82
	E2	10.0	7.86			16.2	13.3			29.6	25.2		
Metconazole	E1	6.41	4.67	-	-	9.50	7.41	-	-	16.1	13.3	-	-
	E2	7.02	5.21	1.12	1.74	10.5	8.30	1.12	1.90	17.9	14.9	1.12	2.14
	E3	11.3	8.97	1.72	8.86	18.7	15.5	1.87	10.8	35.2	30.2	2.03	13.1
	E4	13.3	10.7	1.20	3.26	22.3	18.7	1.20	3.57	42.4	36.5	1.21	3.89
Penconazole	E1	16.0	13.1	1.17	3.44	26.4	22.3	1.18	3.82	48.7	42.1	1.18	4.17
	E2	18.5	15.4			30.8	26.2			57.1	49.5		
Ipcnazole	E1	15.9	13.1	-	-	28.4	24.1	-	-	57.7	50.0	-	-
	E2	16.9	13.9	1.06	1.18	90.1	26.6	1.06	1.31	61.4	53.3	1.07	1.44
	E3	18.2	15.1	1.08	1.47	32.3	27.5	1.08	1.37	65.3	56.8	1.07	1.67
	E4	21.1	17.7	1.18	3.06	37.8	32.5	1.18	3.15	77.3	67.4	1.19	1.94

Table S6. Chromatographic parameters (retention time (t_R)(min), capacity (k) and selectivity factors (α) and resolution (Rs)) obtained for the (enantio)separation of the target fungicides in a solution of 10 mg L⁻¹ of each, by LC-MS/MS on a Lux® 3 μ m i-Cellulose 5 chromatographic column (150 x 2.0 mm, i.d.), under the reverse-elution mode, using a mobile phase composed by 65/35 (v/v) of aqueous 5 mM ammonium hydrogen carbonate/ACN, the column oven temperature set at 25°C, an injection volume of 10 μ L, under different flow rates: 0.25 mL min⁻¹ (a); 0.30 mL min⁻¹ (b); 0.35 mL min⁻¹ (c) and 0.40 mL min⁻¹ (d).

		a (0.25 mL min ⁻¹)				b (0.30 mL min ⁻¹)				c (0.35 mL min ⁻¹)				d (0.40 mL min ⁻¹)			
Fungicide		t_R	k	α	Rs	t_R	k	α	Rs	t_R	k	α	Rs	t_R	k	α	Rs
Fluconazole		2.57	1.27	-	-	2.14	1.27	-	-	1.84	1.28	-	-	1.61	1.28	-	-
Tetraconazole	E1	27.5	23.3	1.08	1.97	23.0	23.5	1.08	1.91	19.8	23.5	1.08	1.76	17.7	23.9	1.08	1.63
	E2	29.6	25.2			24.8	25.3			21.4	25.4			19.0	25.8		
Tebuconazole	E1	27.0	22.9	1.10	1.82	22.6	23.0	1.10	1.78	19.4	23.0	1.10	1.74	17.3	23.3	1.10	1.70
	E2	29.6	25.2			24.7	25.3			21.3	25.3			18.9	25.7		
Metconazole	E1	16.1	13.3	-	-	13.4	13.3	-	-	11.5	13.2	-	-	10.3	13.4	-	-
	E2	17.9	14.9	1.12	2.14	15.0	14.9	1.12	2.24	12.9	14.9	1.13	1.88	11.4	15.1	1.12	1.77
	E3	35.2	30.2	2.03	13.1	29.5	30.4	2.03	13.3	25.4	30.3	2.03	11.5	22.6	30.8	2.05	11.6
	E4	42.4	36.5	1.21	3.89	35.4	36.7	1.21	3.80	30.5	36.6	1.21	3.5	27.2	37.3	1.21	3.45
Penconazole	E1	48.7	42.1	1.18	4.17	40.9	42.5	1.18	3.90	35.2	42.5	1.18	3.73	31.2	43.0	1.18	3.64
	E2	57.1	49.5			48.0	50.0			41.3	50.0			36.6	50.6		
Ipcnazole	E1	57.7	50.0	-	-	48.4	50.5	-	-	41.7	50.5	-	-	36.3	50.6	-	-
	E2	61.4	53.3	1.07	1.44	51.6	53.9	1.07	1.37	44.5	53.9	1.07	1.36	39.1	54.1	1.07	1.39
	E3	65.3	56.8	1.07	0.67	54.9	57.4	1.07	0.71	47.2	57.3	1.06	1.09	41.6	57.4	1.07	1.56
	E4	77.3	67.4	1.19	1.94	64.8	67.9	1.18	2.07	55.7	67.7	1.18	3.32	49.0	68.0	1.18	4.29

Table S7. Experimental conditions applied in the solid-phase extraction (SPE) procedure, indicating the solvents and volumes used in each step (sample pH, column conditioning, washing, and elution).

Initial conditions tested		
	Solvent	Volume (mL)
Matrix (pH)	DW (3, 6.5 (no adjustment) ,10)	500
Conditioning	UPW+ MeOH	10+10
Washing	5% of MeOH in water	10
Elution	MeOH	6
Sample volume optimization		
	Solvent	Volume (mL)
Matrix (pH)	DW (10)	500, 1000, 1500, 2000
Conditioning	UPW+ MeOH	10+10
Washing	5% of MeOH in water	10
Elution	MeOH	6
Conditioning step optimization		
	Solvent	Volume (mL)
Matrix (pH)	DW (10)	500
Conditioning	UPW+ MeOH	10+10, 0+0, 6+6
Washing	5% of MeOH in water	10, 6
Elution	MeOH	6
Elution volume optimization		
	Solvent	Volume (mL)
Matrix (pH)	DW (10)	500
Conditioning	UPW+ MeOH	10+10
Washing	5% of MeOH in water	10
Elution	MeOH	6, 10
Washing step optimization		
	Solvent	Volume (mL)
Matrix (pH)	DW (10)	500
Conditioning	UPW+ MeOH	10+10
Washing	5% of MeOH in water, UPW	10
Elution	MeOH	6
Elution step optimization		
	Solvent	Volume (mL)
Matrix (pH)	DW (10)	500
Conditioning	UPW+ MeOH/ UPW+ EtOH	10+10
Washing	UPW	10
Elution	MeOH/ EtOH	6

Table S8. Retention time, range, coefficient of determination (r^2), instrumental (IDL and IQL) and method (MDL and MQL) limits for fluconazole and the enantiomers/stereoisomers of the chiral 5 target fungicides.

Analyte	Retention time (min)	Range ($\mu\text{g L}^{-1}$)	r^2	IDL ($\mu\text{g L}^{-1}$)	IQL ($\mu\text{g L}^{-1}$)	MDL (ng L^{-1})	MQL (ng L^{-1})
Metconazole E1	10.3	n.a	n.a	n.a	n.a	n.a	n.a
Metconazole E2	11.4	n.a	n.a	n.a	n.a	n.a	n.a
Metconazole E3	22.6	2.01 – 21.8	0.999	0.66	2.01	0.23	0.70
Metconazole E4	27.2	2.35 – 17.9	0.999	0.77	2.35	0.15	0.45
Fluconazole	1.61	0.20 – 400	0.999	0.06	0.18	0.01	0.04
Tetraconazole E1	17.7	3.21 – 200	0.999	1.06	3.21	0.53	1.61
Tetraconazole E2	19.0	3.21 – 200	0.999	1.06	3.21	0.26	0.80
Ipconazole E1	37.2	1.70 – 171	0.999	0.56	1.70	0.28	0.86
Ipconazole E2	39.6	1.82 – 181	0.999	0.60	1.82	0.14	0.43
Ipconazole E3	42.3	3.92 – 26.9	0.999	1.29	3.92	0.86	2.60
Ipconazole E4	49.7	4.43 – 20.6	0.999	1.46	4.43	0.35	1.06
Tebuconazole E1	17.3	3.20 – 200	0.999	1.06	3.20	0.51	1.54
Tebuconazole E2	18.9	3.31 – 200	0.998	1.09	3.31	0.26	0.79
Penconazole E1	31.2	2.16 – 200	0.999	0.71	2.16	0.35	1.05
Penconazole E2	36.6	2.94 – 200	0.999	0.97	2.94	0.24	0.72

Table S9. Diastereoisomeric fraction of metconazole and ipconazole.

Analyte	E1	E2	E3	E4
Metconazole	0.003	0.003	0.541	0.452
Ipconazole	0.441	0.429	0.073	0.058

Table S10. Absolute recovery, extraction efficiency, matrix effect, accuracy, and intra- and inter-batch precision for fluconazole and each enantiomer of the chiral target fungicides.

Analyte	Absolute recovery (%)	Extraction efficiency (%)	Matrix effect (%)	Accuracy (%)	Intra-batch precision (%)	Inter-batch precision (%)
Metconazole E1	n.a	n.a	n.a	111 ± 14.1	6.28 – 6.60	7.18
Metconazole E2	n.a	n.a	n.a	80.3 ± 9.9	4.63 – 6.08	6.45
Metconazole E3	143	101	41.9	90.7 ± 3.2	0.96 – 2.67	4.35
Metconazole E4	128	99.4	28.3	88.2 ± 3.3	1.90 – 2.84	5.34
Fluconazole	57.2	101	-44.2	111 ± 12.6	2.05 – 2.83	8.77
Tetraconazole E1	99.9	98.2	1.63	114 ± 5.5	1.79 – 2.01	3.71
Tetraconazole E2	98.1	99.4	-1.29	108 ± 6.2	2.33 – 3.74	6.15
Ipconazole E1	99.0	93.2	5.80	120 ± 7.2	2.00 – 4.67	5.09
Ipconazole E2	107	100	6.86	118 ± 11.2	2.10 – 4.20	6.98
Ipconazole E3	75.4	75.6	- 0.22	138 ± 21.9	8.07 – 10.6	10.9
Ipconazole E4	105	90.2	14.7	106 ± 13.9	7.72 – 8.45	13.2
Tebuconazole E1	104	103	0.88	132 ± 4.4	1.41 – 3.09	3.35
Tebuconazole E2	102	101	1.09	120 ± 4.8	2.00 – 3.88	4.65
Penconazole E1	103	105	-1.52	128 ± 15.9	1.74 – 2.40	4.29
Penconazole E2	98.5	104	-5.22	119 ± 15.8	2.46 – 3.95	5.38

Table S11. Concentration of each compound in each sample (numbered from 1 to 13), with those not detected referred as ND.

[illegible]

Table S12. Hazard quotient of each compound for adults in each sample (numbered from 1 to 13), with those not detected referred as ND, without expected risk. HQs for the 6 target fungicides (for chiral fungicides, HQ was estimated for the sum of stereoisomeric concentrations) are represented for those compounds detected, where HQ values below 0.1 indicate no expected adverse effect (green). Hazard index (HI) of each sample, sum of the HQs of each compound present in each sample.

[illegible]

Table S13. Hazard quotient of each compound for adults in each sample (numbered from 1 to 13), with those not detected referred as ND, without expected risk. HQs for the 6 target fungicides (for chiral fungicides, HQ was estimated for the sum of stereoisomeric concentrations) are represented for those compounds detected, where HQ values below 0.1 indicate no expected adverse effect (green). Hazard index (HI) of each sample, sum of the HQs of each compound present in each sample.

[illegible]