Insights into fungicide Prothioconazole and its metabolite in wheat: Residue behavior and risk assessment

Qingkui Fang [a,b,1], Zixuan Yan [a,b,1], Chengzhi Zhang [a,b,1], Yanhong Shi [c], Zhaoxian Zhang [c], Quan Gao [a,b], Jinjing Xiao [a,b], Min Liao [a,b], Chuanyong Qi [d], Haiqun Cao [a,b *].

[a] Key Laboratory of Agri-products Quality and Biosafety (Anhui Agricultural University), Ministry of Education, Hefei 230036, China;

[b] Anhui Province Key Laboratory of Integrated Pest Management on Crops, Anhui Agricultural University, Hefei 230036, China;

[c] College of Resources and Environment, Provincial Key Laboratory for Agri-Food Safety, Anhui Agricultural University, Hefei 230036, China;

[d] Hefei Inspection Center for Agricultural Products Quality, Hefei 230091, China.

[*] Corresponding Author: haiquncao@163.com.

[1] The authors contribute equally to this paper.

Table S1. Composition of the nutrient solution

Chemical compound	**Concentration**	**Chemical compound**	**Concentration**
$CuSO_4 \cdot 5H_2O$	0.95 µmol/L	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.05 µmol/L
$MgSO_4 \cdot 7H_2O$	2 mmol/L	KH_2PO_4	1 mmol/L
KNO_3	5 mmol/L	$ZnSO_4.7H_2O$	1 µmol/L
$MnSO_4 \cdot H_2O$	10 µmol/L	$Ca(NO_3)_2 \cdot 4H_2O$	5 mmol/L
Fe (III)-EDTA	50 µmol/L	H_3BO_3	29.6 µmol/L

Table S2. MRM detection conditions for UPLC-MS/MS analysis of prothioconazole and metabolites

Analyte	Scan Mode	Relative molecular mass	Ion pair （m/z）	Transmission power/v	Collision energy/ev
Prothioconazole	ESI^+	344.26	344.09/114.00*	44	26
			344.09/125.06		30
Prothioconazole -desthio	ESI^-	312.22	312.22/89.35*	26	60
			312.22/125.13		34

Table S3. Recovery, coefficient of variation and matrix standard curves of prothioconazole and prothioconazole-dethio spiked in six matrices

Pesticides	Substrate	Spiked (mg/kg)	Recovery rate (%)	RSD (%)	Matrix standard curve	R^2	Matrix effect (%)
Prothioconazole	Nutrient solution	0.05	90.3	2.4	y=83.169x-6.1463	0.999	3.9
		0.2	98.0	2.2			
		0.4	92.5	2.2			
	Root	0.05	93.9	1.2	y=17.909x-46.695	0.999	10.1
		0.2	97.9	3.7			
		0.4	107.6	0.5			
	Stem	0.05	86.5	3.8	y=61.159x+350.58	0.999	23.5
		0.2	78.3	7.1			
		0.4	85.8	7.1			
	Leaf	0.05	81.6	6.5	y=83.479x+438.8	0.999	3.1
		0.2	75.1	4.7			
		0.4	85.1	2.7			
	Wheat grain	0.05	75.8	0.4	y=79.274x+421.4	0.999	4.6
		0.1	78.1	2.0			
		0.2	77.2	9.9			
	Wheat flour	0.05	112.6	2	y=78.251x+618.2	0.999	6.3
		0.1	101.7	3.4			
		0.2	98.0	1.5			
prothioconazole-dethio	Nutrient solution	0.002	112.3	4.8	y=1275.9x-306.84	0.999	2.5
		0.01	98.8	3.8			
		0.05	93.2	3.4			
	Root	0.002	82.3	4.2	y=290.41x+159.94	0.996	8.6
		0.01	87.8	5.2			
		0.05	102.5	3.2			
	Stem	0.002	117.0	4.8	y=1216x-1790.2	0.993	4.6
		0.01	85.9	4.7			
		0.05	98.5	2.1			
	Leaf	0.002	87.0	5.2	y=1018.8x+ 683.57	0.999	20.1
		0.01	96.1	2.2			
		0.05	96.6	2.2			
	Wheat grain	0.01	87.3	4.7	y=1321.7x-416.23	0.999	4.6
		0.05	97.4	7.8			
		0.1	93.5	1.1			
	Wheat flour	0.01	96.8	0.2	y=1450.3x-616.23	0.999	4.4
		0.05	99.1	1.3			
		0.1	86.1	3.6			

Table S4. Primary kinetic parameters of prothioconazole in nutrient solution

Group	Control group				Processing group			
	A	K	T1/2（d）	R^2	A	K	T1/2（d）	R^2
Low concentration	1.343	0.008	3.6	0.955	1.110	0.027	1.06	0.918
High concentration	4.958	0.005	5.7	0.956	6.576	0.011	2.63	0.916

A: Constant；

K: Primary rate constant；

T1/2: Half-life