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Dissipation dynamics and dietary risk assessment of four fungicides as preservatives in pear

Yongfeng Tang[1], Kuikui Hu[1], Xiaomeng Li[1], Chaogang Liu[2], Yanhui Xu[3], Zhaoxian Zhang[1], Xiangwei Wu[1]*

[1] College of Resources and Environment, Anhui Agricultural University, Key Laboratory of Agri-food Safety of Anhui Province, Hefei 230036, China; E-mail: wxw@ahau.edu.cn; xiangweiwu@126.com.
[2] Dangshan Sanlian fruit and vegetable professional cooperative, Tangshan 235300, China; E-mail:755769822@qq.com
[3] Anhui Public Inspection Institute Co., Ltd., Hefei 230051, China; 32596690@qq.com
* Correspondence: Tel/Fax: +86-551-65786320; E-mail: wxw@ahau.edu.cn; xiangweiwu@126.com.

Table S1. Gradient elution program of chromatographic column.

Time (min)	Flow rate (mL/min)	Phase A（%）	Phase B（%）
Initial	0.300	40.0	60.0
0.25	0.300	40.0	60.0
2.00	0.300	10.0	90.0
3.50	0.300	10.0	90.0
3.51	0.300	40.0	60.0
5.00	0.300	40.0	60.0

Table S2. Mass parameters for the analysis of five fungicides.

Fungicides	Parent ion (m/z)	Daughter ion (m/z)	Dwell time (s)	Cone voltage (V)	Collision voltage (V)
Thiophanate-methyl	343	93	0.03	20	46
	343	150.91*	0.03	20	18
Carbendazim	192.1	132.1	0.045	24	28
	192.1	160.1*	0.045	24	18
Pyraclostrobin	388.1	163.0*	0.045	20	25
	388.1	193.9	0.045	20	12
Tebuconazole	308	70.1	0.045	31	22
	308	125*	0.045	31	40
Difenoconazole	406	111.1	0.163	40	60
	406	215.1*	0.163	40	25

*Quantitative ion

Table S3. The information on meteorological conditions during sampling.

Date	Temperature (°C)	Weather	Wind (m/s)
Aug 18, 2021	21-31	Cloudy	2.3
Aug 19, 2021	23-31	Overcast	3.1
Aug 20, 2021	21-25	Cloudy	4.3
Aug 21, 2021	22-30	Cloudy	2.8
Aug 22, 2021	22-27	Light rain	1.9
Aug 23, 2021	21-23	Cloudy	3.4
Aug 24, 2021	20-30	Sunny	2.0
Aug 25, 2021	23-31	Cloudy	4.1
Aug 26, 2021	18-24	Light rain	5.2
Aug 27, 2021	18-21	Cloudy	3.2
Aug 28, 2021	18-23	Light rain	2.5
Aug 29, 2021	20-25	Light rain	2.8
Aug 30, 2021	21-25	Cloudy	2.3
Aug 31, 2021[a]	20-28	Cloudy	2.1

[a] Date of pesticide application and fruit sampling.

Table S4. The fortified recoveries of five fungicides in pears.

Fungicides	Spiked level (mg/kg)	Recovery (%) (n=5)					Average recovery (%)	RSD (%)
		1	2	3	4	5		
Carbendazim	0.01	82.1	101.9	90.6	88.2	89.4	90.4	7.2
	0.1	104.7	104.3	105.4	105.3	112.2	106.4	3.3
	1	94.3	94.1	95.1	94.7	95.3	94.7	0.5
	10	93.2	96.1	94.5	97.5	97.6	95.8	1.9
	50	91.0	90.5	90.6	90.8	94.7	91.5	1.8
Tebuconazole	0.01	89.2	93.3	92.7	88.6	84.7	89.7	3.5
	0.1	92.9	92.8	96.8	95.3	98.6	95.3	2.5
	1	88.2	87.1	85.9	91.4	89.4	88.4	2.1
	10	88.7	87.3	86.9	91.5	90.0	88.9	1.9
	50	84.9	83.6	83.3	84.3	88.2	84.8	2.0
Thiophanate-methyl	0.01	96.6	83.1	99.6	97.6	95.0	94.4	6.5
	0.1	81.1	83.2	73.7	74.4	73.2	77.1	4.7
	1	84.9	89.4	88.2	90.5	89.3	88.5	2.2
	10	90.3	91.5	90.5	95.1	93.6	92.2	2.1
	50	89.8	89.8	90.2	92.5	94.8	91.4	2.2
Pyraclostrobin	0.01	89.9	91.1	90.4	93.0	93.9	91.7	1.7
	0.1	99.1	105.8	105.2	113.7	105.4	105.8	5.2
	1	97.5	106.3	113.3	103.4	102.4	104.6	5.8
	10	97.3	95.7	94.2	97.5	98.0	96.5	1.6
	50	87.0	86.5	88.0	89.0	92.1	88.5	2.2
Difenoconazole	0.01	114.8	109.6	108.4	116.4	108.8	111.6	3.7
	0.1	107.7	110.7	112.9	111.5	117.1	112.0	3.4
	1	95.3	95.7	93.2	97.3	95.7	95.4	1.5
	10	92.2	93.6	90.7	97.5	95.6	93.9	2.7
	50	87.8	86.3	85.1	86.2	90.0	87.1	1.9

Table S5. Residues of the fungicides in pear samples from 18 different refrigerated warehouses

Cold storage	Residue concentration (mg/kg)				
	Carbendazim	Tebuconazole	Thiophanate-methyl	Pyraclostrobin	Difenoconazole
1	0.11±0.02	0.11±0.01	0.02±0.00	0.07±0.01	0.13±0.01
2	0.04±0.00	0.10±0.01	0.01±0.00	0.01±0.00	0.06±0.00
3	0.03±0.01	0.01±0.01	<0.01	<0.01	0.01±0.00
4	0.02±0.01	0.02±0.01	0.01±0.01	<0.01	<0.01
5	0.06±0.03	0.02±0.01	<0.01	0.02±0.00	<0.01
6	0.34±0.01	0.04±0.05	0.02±0.01	0.02±0.01	0.01±0.00
7	0.04±0.02	<0.01	<0.01	0.02±0.00	<0.01
8	0.16±0.01	0.02±0.02	0.01±0.00	<0.01	<0.01
9	14.84±0.36	0.07±0.00	6.22±0.12	0.39±0.02	0.28±0.01
10	4.84±0.26	0.55±0.03	0.03±0.00	0.35±0.03	0.01±0.00
11	11.39±0.27	0.10±0.01	4.83±0.26	0.24±0.01	0.01±0.00
12	3.93±0.10	0.28±0.01	0.06±0.01	0.23±0.01	<0.01
13	11.96±0.86	0.30±0.03	1.40±0.05	0.17±0.01	0.11±0.01
14	16.75±0.62	0.11±0.01	7.35±0.39	0.52±0.05	0.01±0.00
15	30.05±0.75	0.07±0.01	13.55±0.45	<0.01	0.05±0.00
16	12.19±0.81	0.12±0.00	4.48±0.21	0.41±0.03	0.01±0.00
17	11.83±0.40	0.04±0.01	4.50±0.22	<0.01	0.04±0.00
18	7.73±0.46	0.07±0.02	2.98±0.23	0.28±0.01	0.01±0.00
Maximum concentration	30.05	0.55	13.55	0.52	0.28
STRM	3.88	0.07	0.05	0.03	0.01
Positive rate	100.0%	94.4%	83.3%	72.2%	72.2%

Table S6. Residues of the fungicides in commercial pear samples from the supermarket.

Market	Residue concentration (mg/kg)				
	Carbendazim	**Tebuconazole**	**Thiophanate-methyl**	**Pyraclostrobin**	**Difenoconazole**
1	0.10±0.01	0.07±0.00	0.28±0.02	<0.01	0.20±0.01
2	0.06±0.00	<0.01	0.26±0.00	<0.01	0.09±0.00
3	0.26±0.05	0.25±0.04	0.45±0.03	3.36±0.026	0.32±0.05
4	1.03±0.03	0.35±0.01	1.06±0.19	0.97±0.05	0.91±0.03
5	0.41±0.07	0.13±0.01	1.30±0.20	0.55±0.03	0.49±0.06
6	0.07±0.00	<0.01	0.18±0.15	<0.01	0.06±0.00
7	0.07±0.00	<0.01	0.26±0.00	<0.01	0.05±0.00
8	0.08±0..01	<0.01	8.44±1.30	0.40±0.06	0.06±0.00
9	0.10±0.01	0.08±0.01	1.28±0.35	<0.01	0.22±0.04
10	0.17±0.04	0.17±0.01	0.54±0.02	0.58±0.03	0.40±0.04
11	0.08±0.01	<0.01	0.29±0.03	<0.01	0.14±0.02
12	0.10±0.02	0.06±0.00	0.17±0.04	<0.01	0.16±0.00
13	0.40±0.07	0.14±0.00	1.06±0.12	1.55±0.00	0.54±0.01
14	0.14±0.02	0.07±0.04	<0.01	<0.01	0.05±0.00
15	0.07±0.00	<0.01	<0.01	<0.01	0.06±0.00
16	0.07±0.00	<0.01	<0.01	<0.01	0.08±0.00
17	0.08±0.00	0.45±0.05	<0.01	0.46±0.04	0.10±0.01
18	1.36±0.16	2.08±0.27	1.31±0.29	4.93±0.36	7.00±1.14
19	1.11±0.05	1.71±0.05	1.07±0.04	10.12±0.56	2.25±0.31
20	5.68±0.26	1.89±0.13	<0.01	4.26±0.77	2.55±0.34
21	0.38±0.06	0.45±0.03	<0.01	5.06±0.59	1.36±0.43
22	3.05±0.07	0.89±0.06	1.31±0.11	45.93±2.73	1.03±0.08
23	1.74±0.16	1.07±0.20	0.69±0.04	23.47±3.59	23.04±1.77
24	0.21±0.00	0.40±0.04	<0.01	1.86±0.90	1.46±0.33
Maximum concentration	5.68	2.08	8.44	45.93	23.04
STRM	0.16	0.14	0.29	0.51	0.27
Positive rate	100%	70.8%	70.8%	58.3%	100%

Table S7. Dietary intake risk assessment of thiophanate-methyl on the basis of the residues from 18 different refrigerated warehouses.

Food classification	Fi [a]	Reference residue Limit or STMR[b]	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	1	China	0.239900		
Flour and its products	0.1385	0.5	China	0.069250		
Other grains	0.0233					
Tubers	0.0495	0.1	China	0.004950		
Dried beans and their products	0.016					
Dark vegetables	0.0915	3	China	0.274500		
Light vegetable	0.1837	0.5	China	0.091850		
Pickles	0.0103					
Fruits	0.0457	3.88	China	0.177316	ADI×bw[c]	
Nuts	0.0039	0.05	China	0.000195		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.1	China	0.003270		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			0.861231	5.67	15.19%

a Fi referred to the daily intake of a certain agricultural product or food in China (kg),

b STMRi (mg/kg) supervised trials median residue,

c bw was the mean of average body weight of Chinese adult (63 kg).

Table S8. Dietary intake risk assessment of tebuconazole on the basis of the residues from 18 different refrigerated warehouses.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	0.1	China	0.023990		
Flour and its products	0.1385	2	China	0.277000		
Other grains	0.0233	0.05	China	0.001165		
Tubers	0.0495					
Dried beans and their products	0.016					
Dark vegetables	0.0915	2	China	0.183000		
Light vegetable	0.1837	7	China	1.285900		
Pickles	0.0103					
Fruits	0.0457	0.07	China	0.003199	ADI×63	
Nuts	0.0039	0.05	China	0.000195		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	2	China	0.065400		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			1.839849	1.89	97.35%

Table S9. Dietary intake risk assessment of pyraclostrobin on the basis of the residues from 18 different refrigerated warehouses.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	1	China	0.239900		
Flour and its products	0.1385	1	China	0.138500		
Other grains	0.0233	0.05	China	0.001165		
Tubers	0.0495	0.2	China	0.009900		
Dried beans and their products	0.016					
Dark vegetables	0.0915	3	China	0.274500		
Light vegetable	0.1837	5	China	0.91850		
Pickles	0.0103					
Fruits	0.0457	0.03	China	0.001371	ADI×63	
Nuts	0.0039					
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.4	China	0.013080		
Animal oil	0.0087					
Sugar, starch	0.0044	0.4	China	0.000880		
Salt	0.012	0.4	China	0.060000		
Soy sauce	0.009					
Total	1.0286			1.657796	1.89	87.71%

Table S10. Dietary intake risk assessment of difenoconazole on the basis of the residues from 18 different refrigerated warehouses.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	0.5	China	0.119950		
Flour and its products	0.1385	0.1	China	0.013850		
Other grains	0.0233	0.1	China	0.002330		
Tubers	0.0495	0.02	China	0.000990		
Dried beans and their products	0.016					
Dark vegetables	0.0915	2	China	0.183000		
Light vegetable	0.1837	1	China	0.183700		
Pickles	0.0103					
Fruits	0.0457	0.01	China	0.000457	ADI×63	
Nuts	0.0039	0.1	China	0.000390		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.2	China	0.006540		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			0.570067	0.63	90.49%

Table S11. Dietary intake risk assessment of thiophanate-methyl on the basis of the residues from the supermarket pear samples.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	1	China	0.239900		
Flour and its products	0.1385	0.5	China	0.069250		
Other grains	0.0233					
Tubers	0.0495	0.1	China	0.004950		
Dried beans and their products	0.016					
Dark vegetables	0.0915	3	China	0.274500		
Light vegetable	0.1837	0.5	China	0.091850		
Pickles	0.0103					
Fruits	0.0457	0.16	China	0.007312	ADI×63	
Nuts	0.0039	0.05	China	0.000195		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.1	China	0.003270		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			0.691032	5.67	12.19%

Table S12. Dietary intake risk assessment of tebuconazole on the basis of the residues from the supermarket pear samples.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	0.1	China	0.023990		
Flour and its products	0.1385	2	China	0.277000		
Other grains	0.0233	0.05	China	0.001165		
Tubers	0.0495					
Dried beans and their products	0.016					
Dark vegetables	0.0915	2	China	0.183000		
Light vegetable	0.1837	7	China	1.285900		
Pickles	0.0103					
Fruits	0.0457	0.14	China	0.006398	ADI×63	
Nuts	0.0039	0.05	China	0.000195		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	2	China	0.065400		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			1.843048	1.89	97.52%

Table S13. Dietary intake risk assessment of pyraclostrobin on the basis of the residues from the supermarket pear samples.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	1	China	0.239900		
Flour and its products	0.1385	1	China	0.138500		
Other grains	0.0233	0.05	China	0.001165		
Tubers	0.0495	0.2	China	0.009900		
Dried beans and their products	0.016					
Dark vegetables	0.0915	3	China	0.274500		
Light vegetable	0.1837	5	China	0.91850		
Pickles	0.0103					
Fruits	0.0457	0.51	China	0.023307	ADI×63	
Nuts	0.0039					
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.4	China	0.013080		
Animal oil	0.0087					
Sugar, starch	0.0044	0.4	China	0.000880		
Salt	0.012	0.4	China	0.060000		
Soy sauce	0.009					
Total	1.0286			1.679732	1.89	88.87%

Table S14. Dietary intake risk assessment of difenoconazole on the basis of the residues from the supermarket pear samples.

Food classification	Fi (kg)	Reference residue Limit or STMR	Sources	NMDI (mg)	ADI (mg/kg)	Risk quotient (%)
Rice and its products	0.2399	0.5	China	0.119950		
Flour and its products	0.1385	0.1	China	0.013850		
Other grains	0.0233	0.1	China	0.002330		
Tubers	0.0495	0.02	China	0.000990		
Dried beans and their products	0.016					
Dark vegetables	0.0915	2	China	0.183000		
Light vegetable	0.1837	1	China	0.183700		
Pickles	0.0103					
Fruits	0.0457	0.27	China	0.012339	ADI×63	
Nuts	0.0039	0.1	China	0.000390		
Livestock and poultry	0.0795					
Milk and its products	0.0263					
Egg and its products	0.0236					
Fish and shrimp	0.0301					
Vegetable oil	0.0327	0.2	China	0.006540		
Animal oil	0.0087					
Sugar, starch	0.0044					
Salt	0.012					
Soy sauce	0.009					
Total	1.0286			0.581949	0.63	92.37%

Table S15. The Dietary risk assessment (chronic risk) of the five fungicides in pears.

Sources	fungicides	ADI (mg/kg bw)	ARfD (mg/kg bw)	STMRi (mg/kg)	HR (mg/kg)	IEDI (mg/kg bw/day)	NESTI (mg/kg bw)	RQc (%)	RQa (%)
Cold	carbendazim	0.03	0.5	3.88	30.05	2.81E-03	2.18 E-2	9.38	4.36
storage	tebuconazole	0.03	0.03	0.07	0.55	5.08E-05	3.99E-4	0.17	1.33
	thiophanate-methyl,	0.09	0.5	0.05	13.55	3.63E-05	9.83 E-3	0.04	1.97
	pyraclostrobin	0.03	0.05	0.03	0.52	2.18E-05	3.77 E-4	0.07	0.75
	difenoconazole	0.01	0.3	0.01	0.28	7.25E-06	2.03 E-4	0.07	0.07
Market	carbendazim	0.03	0.5	0.16	5.68	1.16E-04	4.12E-3	0.39	0.82
	tebuconazole	0.03	0.03	0.14	2.08	1.02E-04	1.50 E-3	0.34	5.03
	thiophanate-methyl,	0.09	0.5	0.29	8.44	2.10 E-04	6.12 E-3	0.23	1.22
	pyraclostrobin	0.03	0.05	0.51	45.93	3.70 E-04	3.33E-2	1.23	66.63
	difenoconazole	0.01	0.3	0.27	23.04	1.96 E-04	1.67 E-2	1.96	5.57