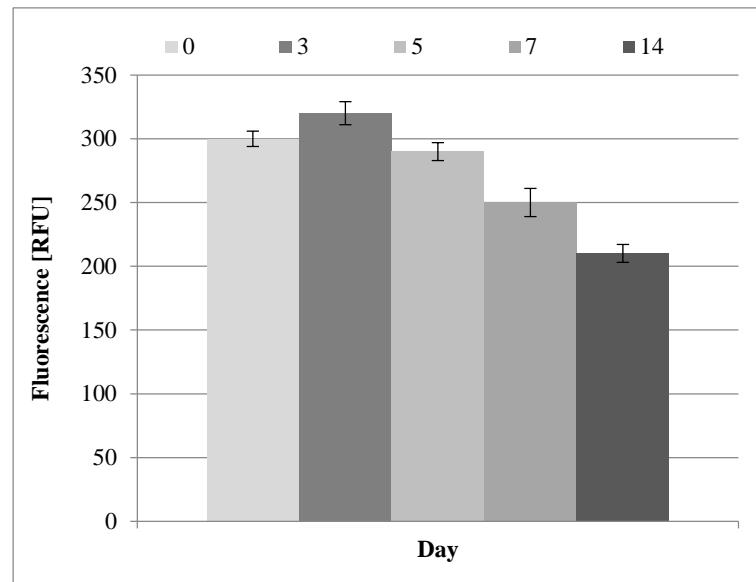
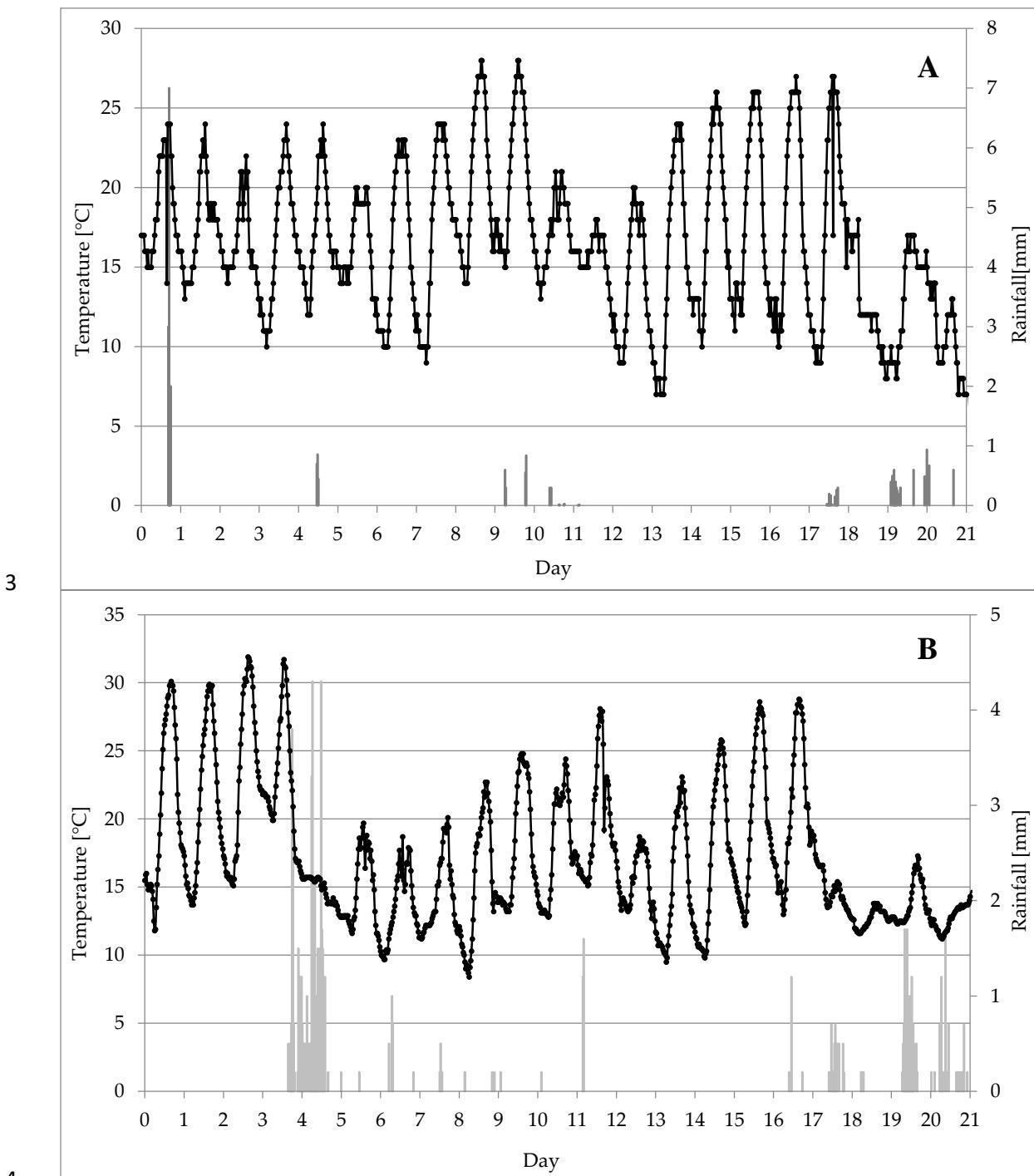


1



2

Figure S1. Bacterial cell viability during 14 days of the experiment



5 **Figure S2.** Temperature and precipitation in a period from 8/16/2017 to 9/6/2017 during the experiment
6 in the Gala variety in Józefów nad Wisłą (A), and from 9/4/2018 to 9/25/2018 during the experiment in
7 the Golden Delicious variety in Rzeszów (B)

8

9 **Table S1.** Method validation parameters: correctness, precision, relative standard deviation, limits of
10 quantification (LOQ); matrix: culture media (BO and PDB) and apples

Active substance	Matrix	Fortification level [mg/kg]	Recovery [%]					Average recoveries [%]	SD [%]	RSD [%]	LOQ [mg/kg]
			I	II	III	IV	V				
Penthiopyrad	BO	1	97.5	105.0	107.0	105.5	102.5	103.5	3.7	3.6	1
		100	117.5	121.0	113.8	113.3	115.5	116.2	3.2	2.7	100
	PDB	1	89.0	88.5	109.5	98.5	102.0	97.5	8.9	9.2	1
		100	112.8	115.0	112.5	109.0	107.8	111.4	3.0	2.7	100
Apples	Apples	0.01	118.0	118.5	117.0	112.5	110.0	115.2	3.7	3.3	0.01
		1	115.5	113.5	109.0	105.0	112.5	111.1	4.1	3.7	0.01

11

12 **Table S2.** Validation parameters - linearity, matrix: culture media (BO and PDB) and apples

Active substance	Matrix	No. of fortification levels	Linearity [mg/kg]	Calibration curve equation $y = ax + b$		Coefficients of determination
				a	b	
	BO	5	0.004-0.4	348.9	20.8	0.9902
Penthiopyrad	PDB	5	0.004-0.4	443.2	28.2	0.9901
	Apples	5	0.01-1	32915.6	8.1	0.9983

13

14 **Table S3.** Acquisition parameters of a liquid chromatograph with an ion trap mass detector (MRM
15 mode) used for patulin determination

Flow rate	1 mL/min
Injection volume	5 µL
Mobile phases:	
A	methanol/water/acetic acid 10/89/1 (v/v/v)
B	methanol/water/acetic acid 97/2/1 (v/v/v)
	(both phases contained 5 mmol/L ammonium acetate)
Gradient	0 % B for 2.0 min 50 % B from 2.0 to 5.0 min 100% B from 5.0 to 6.0 min 100 % B to 7.0 min, then 0 % B to 12 min
Curtain gas	30 psi
Ionspray voltage / temperature	-4500 V / 550°C
Ion source gas 1	60 psi
Ion source gas 2	60 psi

16

17 **Table S4.** MRM transitions for patulin and an internal standard, and mass spectrometer operating
18 conditions

Ionization	Precursor ion	Product ions	Declustering potential	Collision energy	Cell exit potential
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	[m/z]	[m/z]	[V]	[V]	[V]
Patulin	[M-H] ⁻	153.0	109.1/81.0	-85	-12/-16
13C-Patulin	[M-H] ⁻	160.0	115.0/86.1	-95	-12/-16

19

Table S5. Acquisition parameters of a liquid chromatograph with a mass detector (MRM mode) used for trichothecenes and zearalenone determinations

Flow rate	0.5 mL/min
Injection volume	7 µL
Mobile phases:	
A	1% CH ₃ COOH in H ₂ O
B	methanol
(both phases contained 5 mM CH ₃ COONH ₄)	
Gradient	
	30 % B for 0.5 min
	90 % B from 0.5 to 6.0 min
	90 % B to 10.0 min, then
	30 % B to 15 min
Curtain gas	25 psi
Collision gas	6 psi
Ionspray voltage /temperature	-4000 V (negative polarity); 5000 V (positive polarity) / 500°C
Ion source gas 1	50 psi
Ion source gas 2	50 psi

22

Table S6. MRM transitions for trichothecenes, zearalenone, and an internal standard, and mass spectrometer acquisition parameters

	Ionization	Precursor ion [m/z]	Product ions [m/z]	Declustering potential [V]	Collision energy [V]	Cell exit potential 1 [V]
13C-Deoxynivalenol	[M+Ac] ⁻	370.2	310.0	-50	-14	-7
13C-HT-2 Toxin	[M+NH ₄] ⁺	464.1	278.1	51	17	18
13C-T-2 Toxin	[M+NH ₄] ⁺	508.3	322.1	61	19	8
13C-Zearalenone	[M-H] ⁻	335.1	139.9	-100	-42	-7
Deoxynivalenol	[M+Ac] ⁻	355.1	264.8/58.9	-35	-20/-38	-17/-1
Diacetoxyscirpenol	[M+Ac] ⁻	384.1	307.0/247.0	51	17/19	20/16
HT-2 Toxin	[M+NH ₄] ⁺	442.2	215.0/263.0	51	19/17	14/18
Nivalenol	[M+Ac] ⁻	371.1	281.0/59.0	-40	-22/-40	-14/-5
T-2 Toxin	[M+NH ₄] ⁺	484.1	215.0/185.0	61	25/29	14/12
Zearalenone	[M-H] ⁻	317.1	130.8/174.9	-85	-40/-32	-7/-9

25