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SUPPLEMENTARY MATERIALS

Understanding How Physicochemical Properties of Mancozeb and Metalaxyl Shape Onion (*Allium cepa* L.) Production Outcomes: Experimental Stability Studies and Molecular Modeling

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Materials and Methods

Chemicals and solutions

Other used chemicals were H_3PO_4 (85%, Sigma–Aldrich, Germany) and acetonitrile (ACN, 99.9%, Sigma–Aldrich, Germany), HCl (0.1 mol/dm^3), HCl solution (1: 1), H_2SO_4 (0.5 mol/dm^3), cc NH_3, NaOH (1.0 mol/dm^3), Mg–EDTA (0.005 mol/dm^3), EDTA $C_{10}H_{14}N_2O_8Na_2 \times 2H_2O$ (0.01 mol/dm^3), $AgNO_3$ (0.01 mol/dm^3), KCl (0.01 mol/dm^3), Fe(III) solution (0.1000 g/dm^3), K_2CrO_4 aqueous solution (5%), H_2O_2 aqueous solution (3%), KSCN aqueous solution (20%), solid hydroxylamine hydrochloride $NH_2OH \times HCl$, ammonia buffer NH_3–NH_4Cl (pH 10), aqueous methyl orange solution (0.1%), and solid solution sodium chloride/eriochrome black-T (0.5%).

Degradation procedures in the sun simulator

Direct photolysis was carried out using the Sun 2000 simulator, model 11016-1, from ABET Technologies. The simulator is equipped with a 550 W Xe short arc lamp and a built-in AM 1.5G filter that converts the xenon lamp radiation into normalized AM1.5G light, i.e., corrects the output of a xenon lamp to better match the global solar spectrum when the sun is at a zenith angle of 48.0°. This model also has a 280–400 nm dichroic reflector that enables output radiation in the UV part of the spectrum, and accelerated UV aging tests can be carried out. The illumination area is up to 100×100 mm, and the nominal working distance was between 100 and 610 mm.
Experiments were performed using 30 cm^3 of mancozeb and metalaxyl mixture. Before irradiation, the photochemical cell was placed on a magnetic stirrer. The stirrer was positioned at a distance of 280 mm underneath the sun simulator. The samples were irradiated for 120 min. A UV light (UVA+UVB) intensity of 95 W/m^2 was measured with the UV radiometer VLX-3W.
HelioClim-3 service provides UV-A (315–400 nm), UV-B (280–315 nm), and UV total (UV-A+UV-B) irradiation values in Wh/m2 computed from the satellite-derived solar radiation database HelioClim-3 version 5 over a horizontal plane.

Analytical procedures

To monitor the removal kinetics of mancozeb and metalaxyl from water, aliquots (0.5 cm^3) of the reaction mixture were taken before the beginning of irradiation, and at certain time intervals during irradiation (the total sampled volume did not exceed 10% of the initial volume). Samples were injected and analyzed using UFLC−PDA, equipped with an Eclipse XDB−C18 column (150 mm × 4.6 mm i.d., particle size 5 μm, 30 °C). When recording the chromatograms of mancozeb and metalaxyl, the mobile phase ACN : 0.1% H_3PO_4 was used. Isocratic elution (ACN : 0.1% H_3PO_4, 50 : 50, *v*/*v*) at a flow rate of 1.0 cm^3/min, sample volume of 20 μL, was used. Chromatograms were recorded at the wavelength of the maximum absorbance of mancozeb (λ_{max} = 234 nm), with a retention time of (2.0 ± 0.1) min, and metalaxyl (λ_{max} = 216 nm), with a retention time of (7.0 ± 0.1) min.

During the degradation process, a combination glass electrode (pH-Electrode SenTix 20, WTW) connected to a pH meter (pH/Cond 340i, WTW) was used to monitor the initial pH values and their changes. The radiation energy flux was measured using a Delta Ohm HD 2102.2 (Padova, Italy) radiometer, which was fitted with the LP 471 UV (spectral range 315 – 400 nm).

Determination of the total hardness of the water. An aliquot of 50.00 cm^3 of the water sample was measured into an Erlenmeyer flask. By adding cc NH_3 in drops, the pH was adjusted from neutral to 10, after which 30 mg of $NH_2OH \times HCl$ and 4 cm^3 of NH_3 – NH_4Cl buffer were added. The solution was stirred, and 0.20 g of eriochrome black-T indicator was added and titrated with 0.01 mol/dm^3 EDTA solution until the indicator color changed from purple to blue. The same procedure was repeated two more times.

Determination of chloride in water. An aliquot of 50.00 cm^3 water sample was measured into an erlenmeyer flask. Then 1.0 cm^3 of 5% K_2CrO_4 solution was added and titrated with 0.01 mol/dm^3 $AgNO_3$ solution until a red-brown color appeared. The same procedure was repeated two more times.

Determination of iron content in water. An aliquot of 100.00 cm^3 water sample was measured into a porcelain evaporation cup. The sample was evaporated to 30.00 cm^3 and quantitatively transferred into a 100.00 cm^3 measuring flask. Then 3.00 cm^3 of HCl (1: 1), 2.00 cm^3 of 3% H_2O_2 solution, and 5.00 cm^3 of 20% KSCN solution were added. The flask was filled with ultrapure water and well shaken. The calibration curve was constructed (Figure S1). The obtained correlation coefficient was r = 0.999. Iron concentration was determined by measuring the absorbance of the formed iron complex at 510 nm on a double-beam T80+UV-vis Spectrometer.

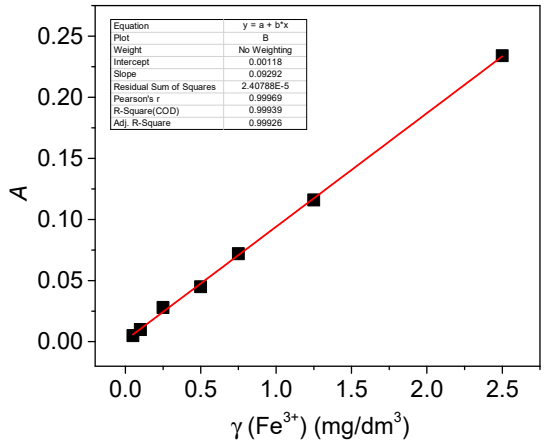


Figure S1. Calibration curve for the determination of iron.

Determination of sodium content in water. An aliquot of 100.00 cm^3 water sample was measured into a porcelain evaporation cup. The sample was evaporated to 20.00 cm^3 and quantitatively transferred into a 50.00 cm^3 measuring flask. Then, 5.00 cm^3 of concentrated HCl was added. The flask was filled with ultrapure water and well shaken. The calibration curve was constructed (Figure S2). The obtained correlation coefficient was r = 0.982. Sodium concentration was determined by measuring the photocurrent of the formed sodium cation on an FP910 Flame Photometer.

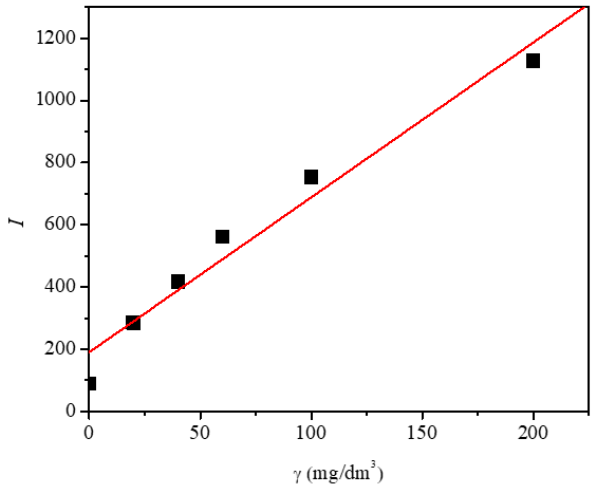


Figure S2. Calibration curve for the determination of sodium.

Determination of potassium content in water. An aliquot of 100.00 cm³ water sample was measured into a porcelain evaporation cup. The sample was evaporated to 20.00 cm³ and quantitatively transferred into a 50.00 cm³ measuring flask. Then, 5.00 cm³ of concentrated HCl was added. The flask was filled with ultrapure water and well shaken. The calibration curve was constructed (Figure S3). The obtained correlation coefficient was $r = 0.987$. Potassium concentration was determined by measuring the photocurrent of the formed potassium cation on an FP910 Flame Photometer.

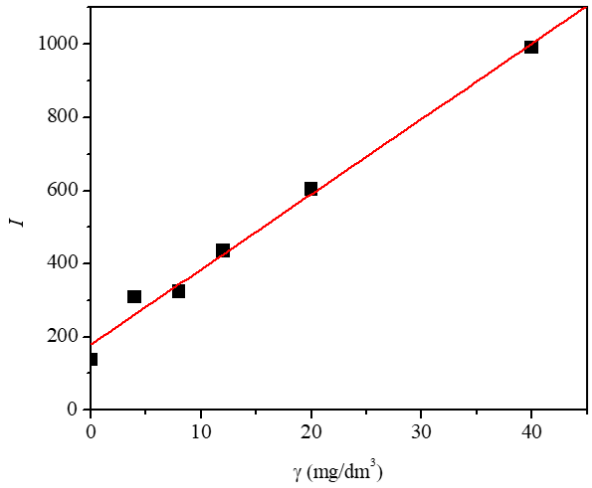


Figure S3. Calibration curve for the determination of potassium.

Determination of water conductivity. A 0.01 mol/dm³ KCl solution was used to calibrate the conductometric cell. The calibration curve was obtained (Figure S4) with a good correlation coefficient, $r = 0.999$. The conductometric cell was then immersed in a water sample, and the conductivity was determined. The same procedure was repeated for other water samples.

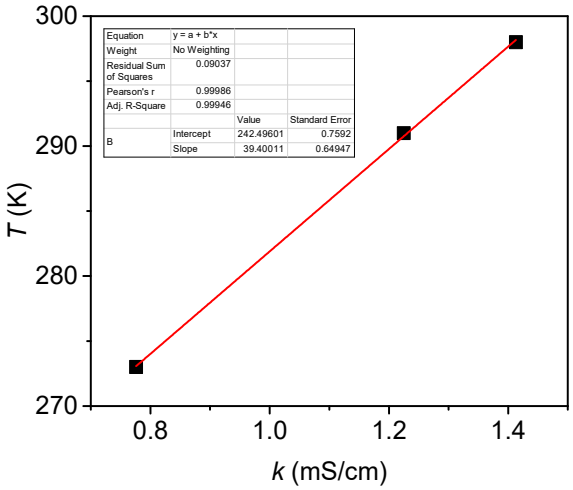


Figure S4. Calibration curve for the determination of the conductivity of a standard KCl solution at different temperatures.

Results and Discussion

Table S1. The physicochemical characteristics of the analyzed ultrapure water and rainwater.

Parameter	Water type	
	Ultrapure water	Rainwater
TH[1] (mg $CaCO_3/dm^3$)	0.00	9.01
TH (°d)	0.00	0.50
Chloride ion (mg/dm^3)	1.82	3.15
Iron ion (mg/dm^3)	0.00	0.00
Sodium ion (mg/dm^3)	1.55	1.90
Potassium ion (mg/dm^3)	1.60	1.80
pH	7.87	7.66
CDY[2] at 25 °C (mS/cm)	0.001	0.022

[1]Total hardness, [2]Conductivity.

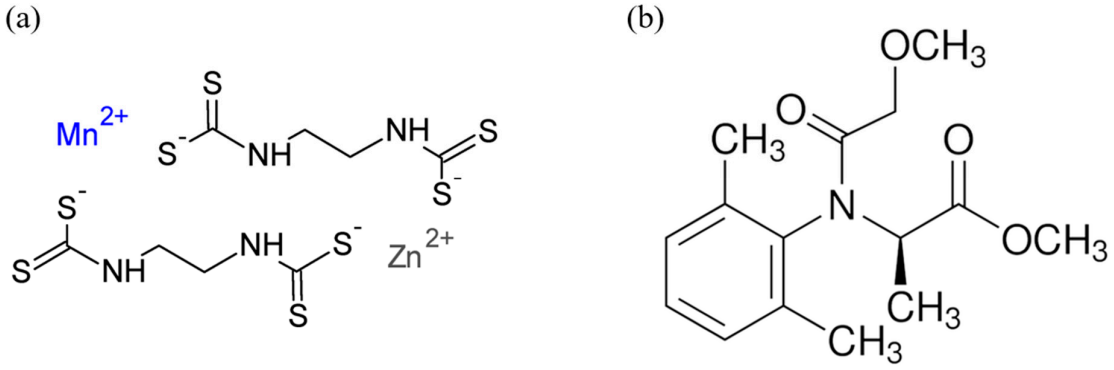
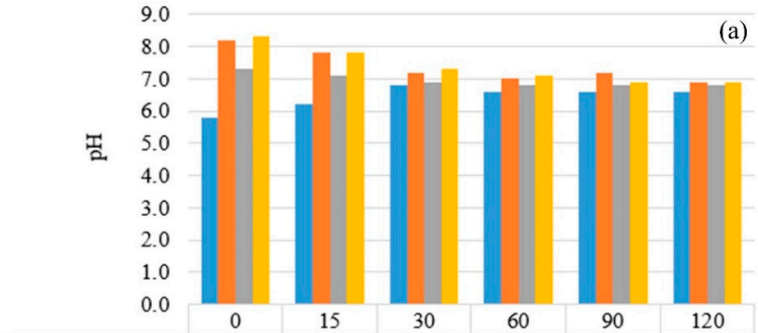
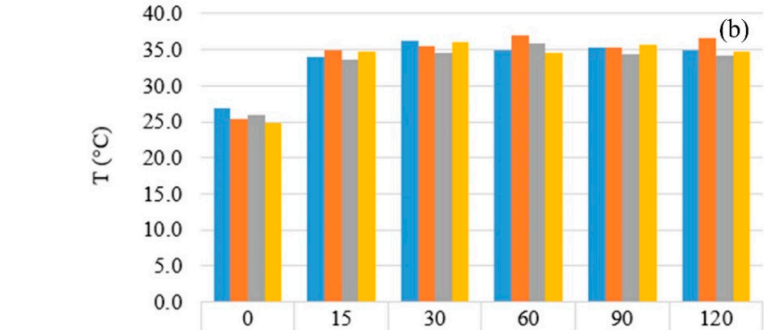


Figure S5. The structural formula of mancozeb (a) and metalaxyl (b).

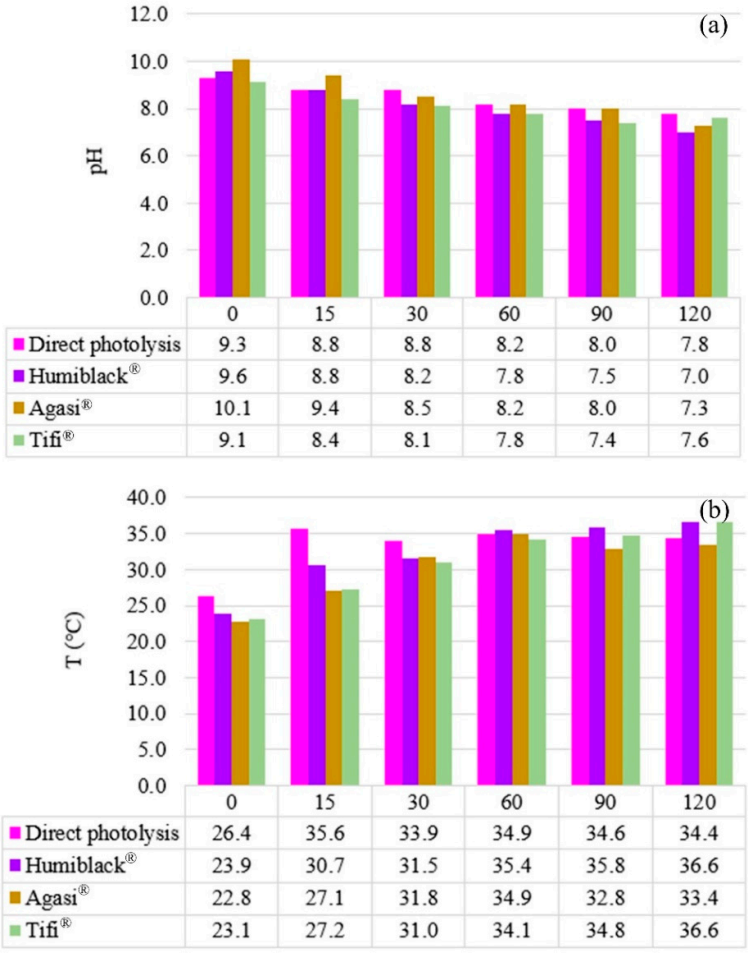


	0	15	30	60	90	120
Direct photolysis	5.8	6.2	6.8	6.6	6.6	6.6
Humiblack®	8.2	7.8	7.2	7.0	7.2	6.9
Agasi®	7.3	7.1	6.9	6.8	6.8	6.8
Tifi®	8.3	7.8	7.3	7.1	6.9	6.9



	0	15	30	60	90	120
Direct photolysis	26.9	33.9	36.2	35.0	35.2	34.9
Humiblack®	25.4	34.9	35.4	36.9	35.3	36.6
Agasi®	26.0	33.7	34.5	35.8	34.4	34.2
Tifi®	24.9	34.8	36.1	34.5	35.7	34.7

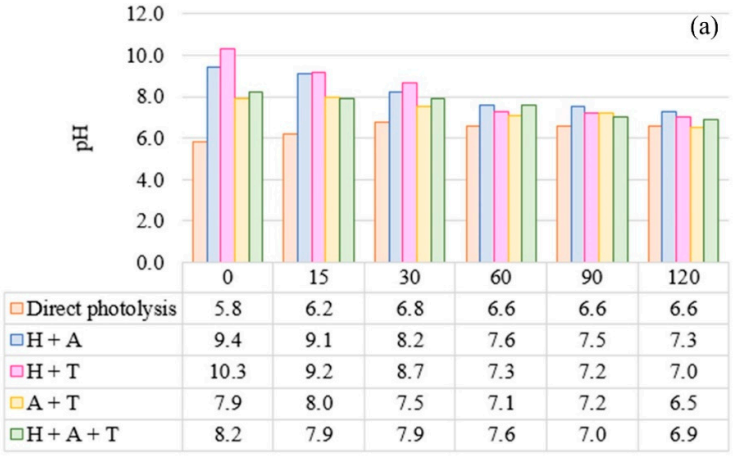
Figure S6. Change of the (a) pH and (b) T (°C) during direct photolysis of mancozeb and metalaxyl in ultrapure water under the influence of Humiblack®, Agasi®, and Tifi®.



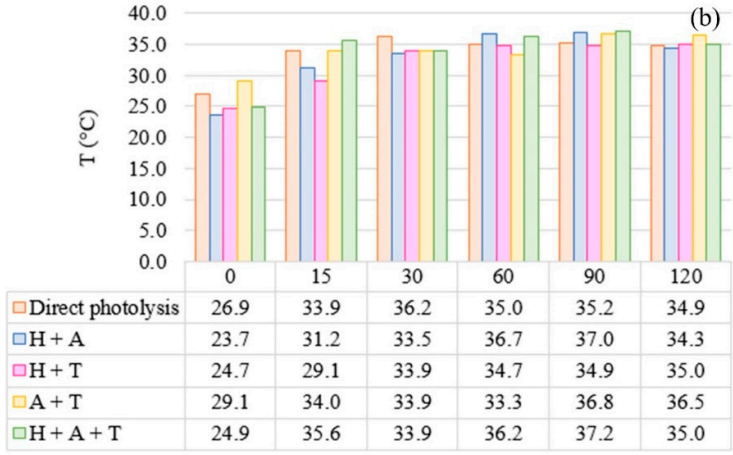
	0	15	30	60	90	120
Direct photolysis	9.3	8.8	8.8	8.2	8.0	7.8
Humiblack®	9.6	8.8	8.2	7.8	7.5	7.0
Agasi®	10.1	9.4	8.5	8.2	8.0	7.3
Tifi®	9.1	8.4	8.1	7.8	7.4	7.6

	0	15	30	60	90	120
Direct photolysis	26.4	35.6	33.9	34.9	34.6	34.4
Humiblack®	23.9	30.7	31.5	35.4	35.8	36.6
Agasi®	22.8	27.1	31.8	34.9	32.8	33.4
Tifi®	23.1	27.2	31.0	34.1	34.8	36.6

Figure S7. Change of the (a) pH and (b) T (°C) during direct photolysis of mancozeb and metalaxyl in rainwater under the influence of Humiblack®, Agasi®, and Tifi®.

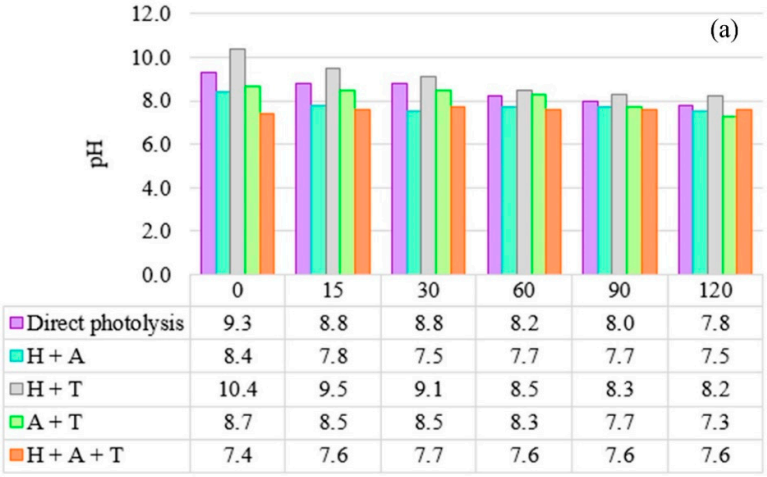


	0	15	30	60	90	120
Direct photolysis	5.8	6.2	6.8	6.6	6.6	6.6
H + A	9.4	9.1	8.2	7.6	7.5	7.3
H + T	10.3	9.2	8.7	7.3	7.2	7.0
A + T	7.9	8.0	7.5	7.1	7.2	6.5
H + A + T	8.2	7.9	7.9	7.6	7.0	6.9

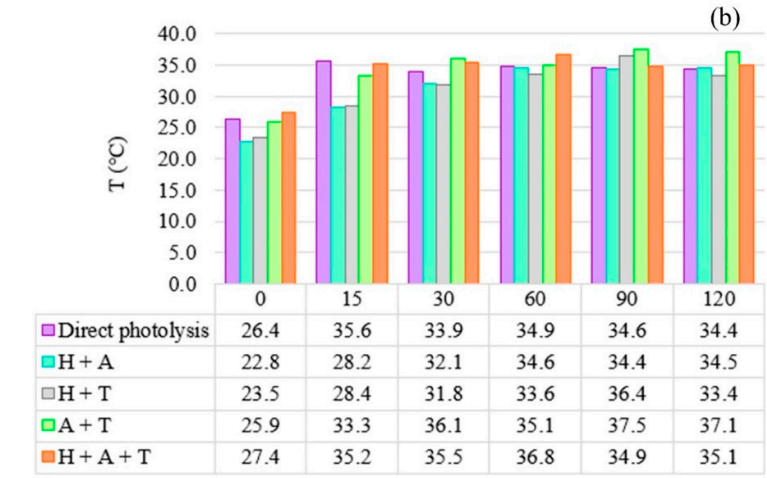


	0	15	30	60	90	120
Direct photolysis	26.9	33.9	36.2	35.0	35.2	34.9
H + A	23.7	31.2	33.5	36.7	37.0	34.3
H + T	24.7	29.1	33.9	34.7	34.9	35.0
A + T	29.1	34.0	33.9	33.3	36.8	36.5
H + A + T	24.9	35.6	33.9	36.2	37.2	35.0

Figure S8. Change of the (a) pH and (b) T (°C) during direct photolysis of mancozeb and metalaxyl in ultrapure water under the influence of Humiblack® (H), Agasi® (A), and Tifi® (T) mixture.



	0	15	30	60	90	120
Direct photolysis	9.3	8.8	8.8	8.2	8.0	7.8
H + A	8.4	7.8	7.5	7.7	7.7	7.5
H + T	10.4	9.5	9.1	8.5	8.3	8.2
A + T	8.7	8.5	8.5	8.3	7.7	7.3
H + A + T	7.4	7.6	7.7	7.6	7.6	7.6



	0	15	30	60	90	120
Direct photolysis	26.4	35.6	33.9	34.9	34.6	34.4
H + A	22.8	28.2	32.1	34.6	34.4	34.5
H + T	23.5	28.4	31.8	33.6	36.4	33.4
A + T	25.9	33.3	36.1	35.1	37.5	37.1
H + A + T	27.4	35.2	35.5	36.8	34.9	35.1

Figure S9. Change of the (a) pH and (b) T (°C) during direct photolysis of mancozeb and metalaxyl in rainwater under the influence of Humiblack® (H), Agasi® (A), and Tifi® (T) mixture.