Supplementary Material

Photophysical and photochemical insights into the photodegradation

of tricyclazole and pymetrozine in water bodies of a rice field

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S1 Analysis methods for water constituents

Dissolved organic carbon (DOC) was measured by a Liquid TOC II analyzer (Elementar, Germany) after water samples were acidified with 2 M HCl, and the detection limit for TOC was 0.66 mg C/L. F^-, Cl^-, Br^-, NO_2^-, NO_3^- and SO_4^{2-} were determined by ion chromatography (IC6000, Wanyi Ltd., Anhui, China). Total soluble iron concentrations were assayed through the reduction of Fe^{3+} to Fe^{2+} by hydroxylamine-HCl, and Fe^{2+} was measured by the ferrozine analytical method at 562 nm (Stookey 1970). Absorbance spectra of water samples were acquired on an UV-2600 PC spectrophotometer (Shunyuhengping Ltd., Shanghai, China). Total alkalinity (as $CaCO_3$) was determined by the titration method according to National Standards of the People's Republic of China (GB 7477-87) (China 1987). Dissolved oxygen (DO) was measured by Winkler-method (Künnemann and Bashamohideen 1978).

S2 Methods for calculating optical parameters

Filtered water absorbance were collected between 200 and 800 nm. Light screen factors were calculated ($S_{\sum\lambda,\text{range}}$) via the following equation (Equation S1 and S2) (Janssen and McNeill 2015, Williams *et al.* 2018):

$$S_\lambda = \frac{1-10^{-\alpha_\lambda l}}{2.303\alpha_\lambda l} = \frac{1-10^{-A_\lambda}}{2.303A_\lambda} \qquad \text{Equation S1}$$

$$S_{\sum\lambda,\text{range}} = \sum_\lambda S_\lambda = \sum_\lambda \frac{1-10^{-A_\lambda}}{2.303A_\lambda} \qquad \text{Equation S2}$$

where S_λ is the light screen factor at wavelength λ, α_λ is the light attenuation coefficient at wavelength λ, and l is the path length. Light screen factors for modeling the direct photolysis of tricyclazole (TRI) and pymetrozine (PYM) in different water bodies were estimated with l=5 cm.

The ratio of the absorbance at λ = 250 nm over the absorbance at λ = 365 nm is defined as the $E2/E3$ ratio (Dalrymple *et al.* 2010). The specific ultraviolet absorbance values at the wavelength λ = 254 nm (SUVA$_{254}$, unit L mg C^{-1} m^{-1}) of the DOM solutions was calculated by dividing the absorbance by the optical path length and carbon concentration (Weishaar *et al.* 2003).

S3 Methods for measuring leaf area

Four to six plants were randomly collected during each investigation. The leaves from individual plants were cut down and the profile of each leaf was drawn on graph paper with grid areas of 1 mm × 1 mm. The leaf area was calculated by counting the number of grids, and leaf area index (LAI) is defined as the total area of leaves of individual plant per unit horizontal ground area.

S4 Methods for determining k_{obs} and k_{ROSs}

The photolysis of pesticides assumed pseudo-first-order kinetics with an observed rate constant (k_{obs}) and half life ($T_{1/2}$) calculated as shown in Equation S3 and S4.

$$k_{obs} = \ln(C_t / C_o) \qquad \text{Equation S3}$$

$$T_{1/2} = \ln 2 / k_{obs} \qquad \text{Equation S4}$$

$k_{^1O_2,\text{Pesticide}}$ was determined by illuminating the solution with 40 μM Rose Bengal (RB) as the photosensitizer. The light was filtered with 0.5% $K_2Cr_2O_7$ to remove light with wavelength < 500 nm. Aliquots of the solutions were removed at various time points and analyzed by HPLC. The loss of the FFA, tricyclazole (TC), and pymetrozine (PYM) was recorded, and the reaction rate constant of specific pesticides with $^1O_2$ was obtained as shown in Equation S5 ($k_{^1O_2,\text{FFA}} = 1.00 \times 10^8$ M^{-1} s^{-1}) (Appiani *et al.* 2017).

$$\frac{\ln[\text{FFA}]_t}{\ln[\text{FFA}]_0} = \frac{k_{^1O_2,\text{FFA}}}{k_{^1O_2,\text{Pesticide}}} \frac{\ln[\text{Pesticide}]_t}{\ln[\text{Pesticide}]_0} \qquad \text{Equation S5}$$

Fenton solutions containing 33 μM $FeSO_4$ and 300 μM H_2O_2 were used to yield $HO^\bullet$. The initial concentrations of benzoic acid (BA) was 100 μM that competitively reacted with $HO^\bullet$ in solutions contain 100 μM TC or 40 μM PYM. The loss of the BA, TRI, and PYM was recorded, and the reaction rate constant was obtained as shown in Equation S6 with $k_{HO^\bullet,\text{BA}} = 5.9 \times 10^9$ M^{-1} s^{-1} (Buxton *et al.* 1988).

$$\frac{\ln[\text{BA}]_t}{\ln[\text{BA}]_0} = \frac{k_{HO^\bullet,\text{BA}}}{k_{HO^\bullet,\text{Pesticide}}} \frac{\ln[\text{Pesticide}]_t}{\ln[\text{Pesticide}]_0} \qquad \text{Equation S6}$$

S5 HPLC parameters for analysis

The concentrations of all chemicals including *p*-nitroanisole (PNA), and probes for measuring ROS as well as two pesticides (TC and PYM) were determined by Agilent 1260 series high-performance liquid chromatography (HPLC) with a variable wavelength detector (VWD) and fluorescence detector (FLD), and an Agilent C18 column (3.0×150 mm, 3.5μm particle diameter) was used for chromatographic separations at 30°C. The detection limits for TC and PYM were 0.063 and 0.018 μM, respectively. The initial concentrations of PNA, FFA, SA and TPA in prepared solutions were 10, 100, 100, and 500 μM. Instrument parameters for analysis of different chemicals are summarized as follows:

Chemicals	Mobile phase	Detector	Detection wavelength*
PNA	Methanol:H_2O=65:35	VWD	λ_{abs}=300 nm
FFA	Methanol:H_2O=10:90	VWD	λ_{abs}=219 nm
HAD	Acetonitrile:Acetate (15 mM)=15:85	VWD	λ_{abs}=254 nm
hTPA	Methanol:Formic acid (0.1%)=35:65	FLD	λ_{ex}=315 nm, λ_{em}=425 nm
TC	Methanol:H_2O=30:70	VWD	λ_{abs}=220 nm
PYM	Methanol:H_2O=45:55	VWD	λ_{abs}=298 nm

*λ_{abs} presents absorption wavelength corresponds to the analysis with VWD; λ_{ex} and λ_{em} present excitation and emission wavelength correspond to the analysis by FLD.
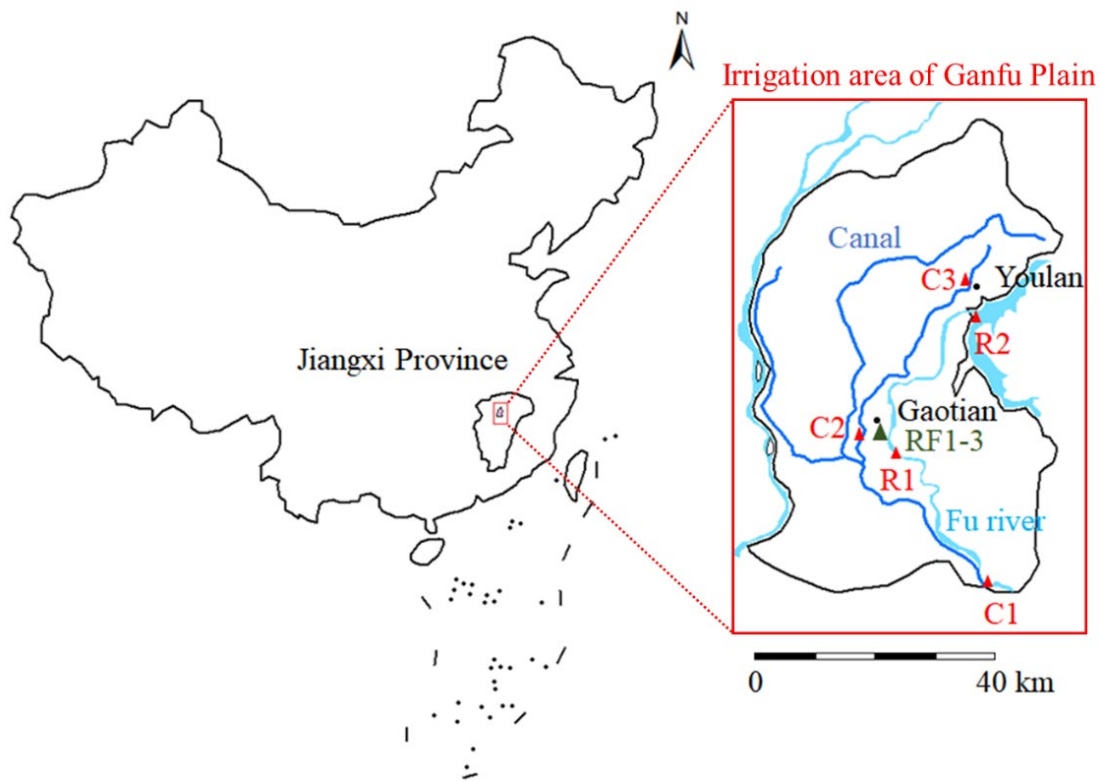
Figure S1. Sketch map of the Ganfu Plain Irrigation Area (Sampling locations: RF represents the rice field, C represents the canal, and R represents the Fu River)
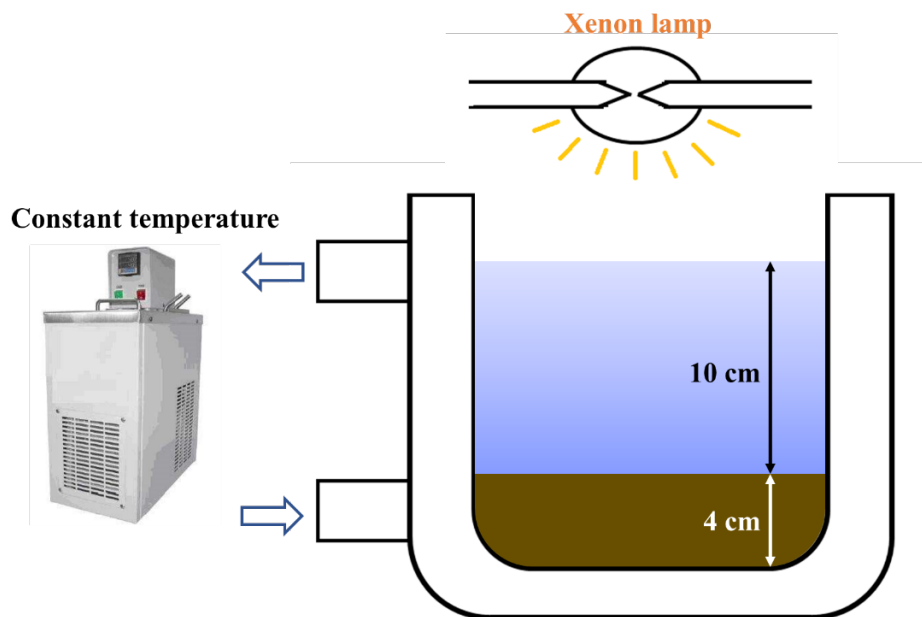

Figure S2. Schematic diagram of the experimental settings for the center composite design
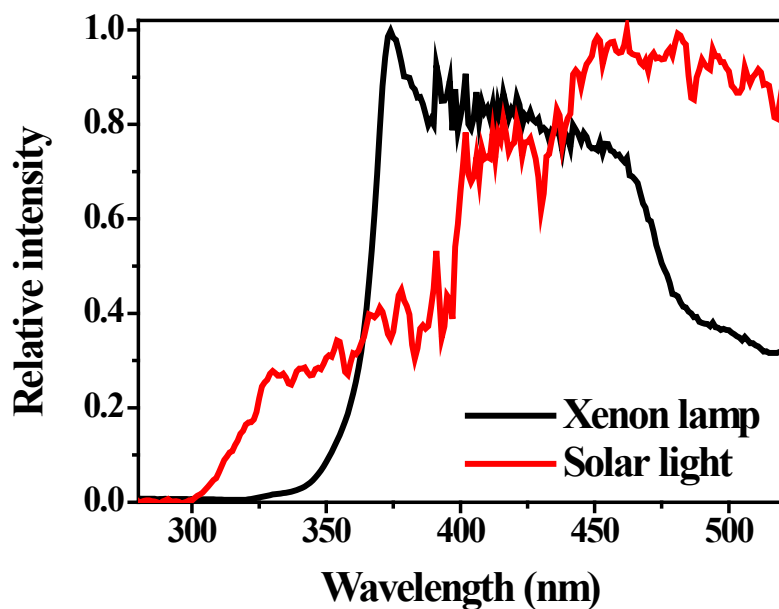
Figure S3. Relative intensity of the irradiance spectrum for xenon lamp and solar light
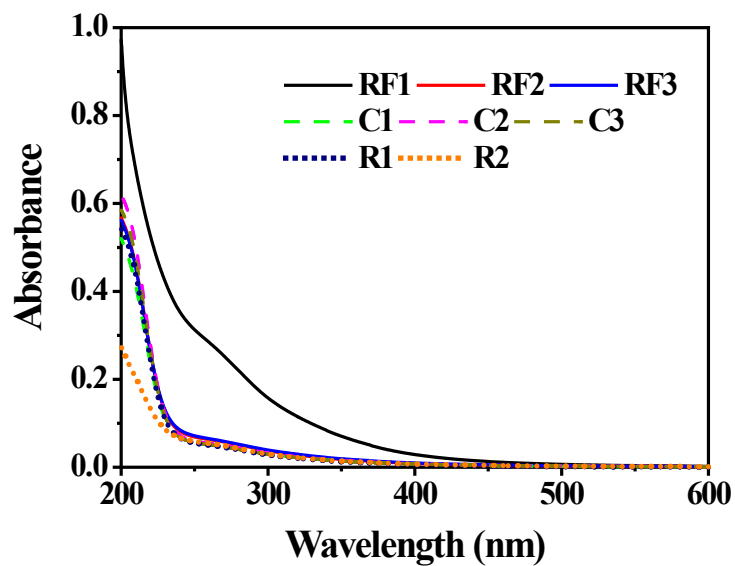

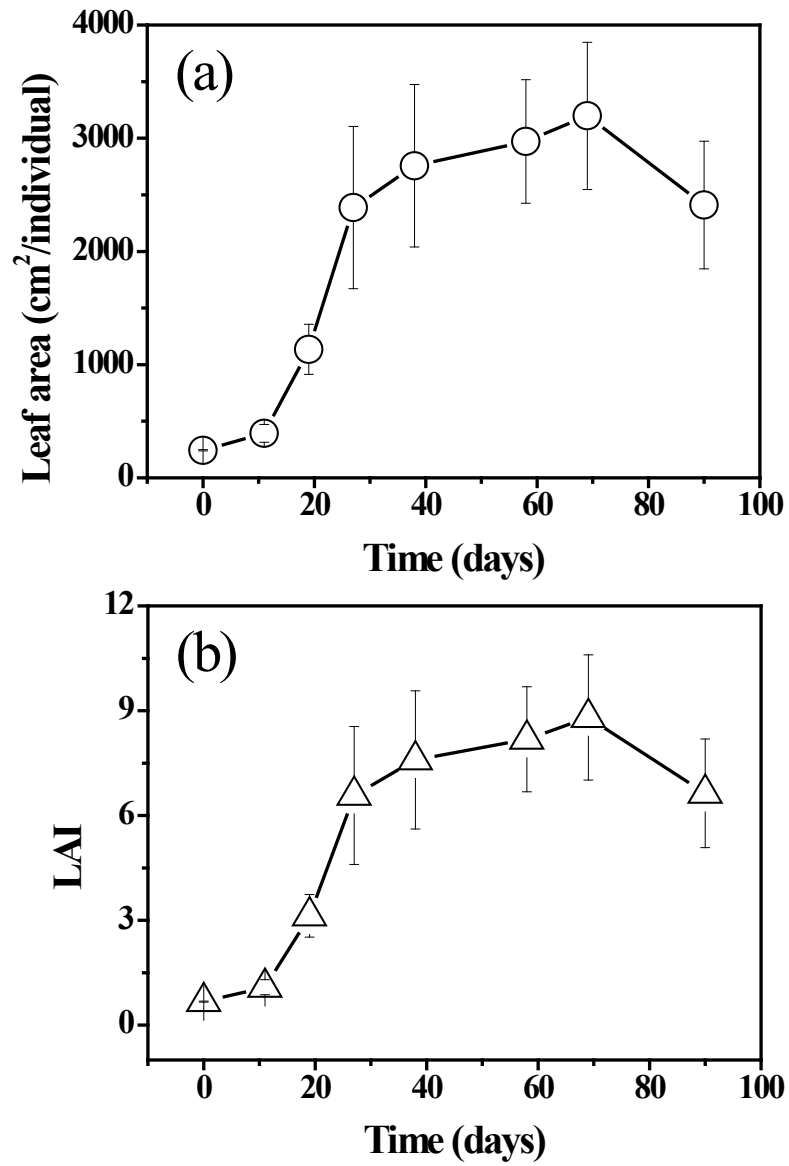Figure S4. Absorbance spectra of 8 surface water samples

Figure S5. The variation of (a) leaf area, and (b) leaf area index (LAI) of rice as a function of growing time after transplanting
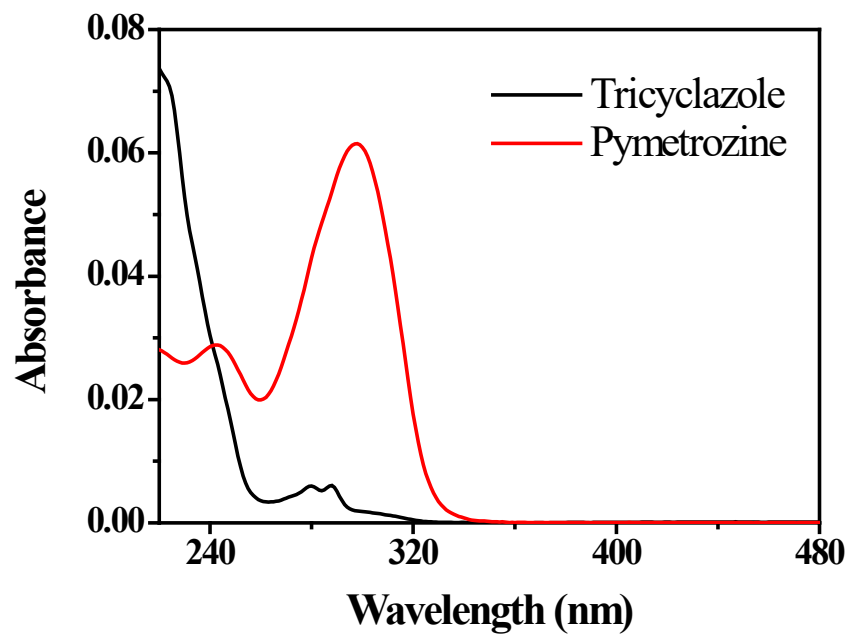
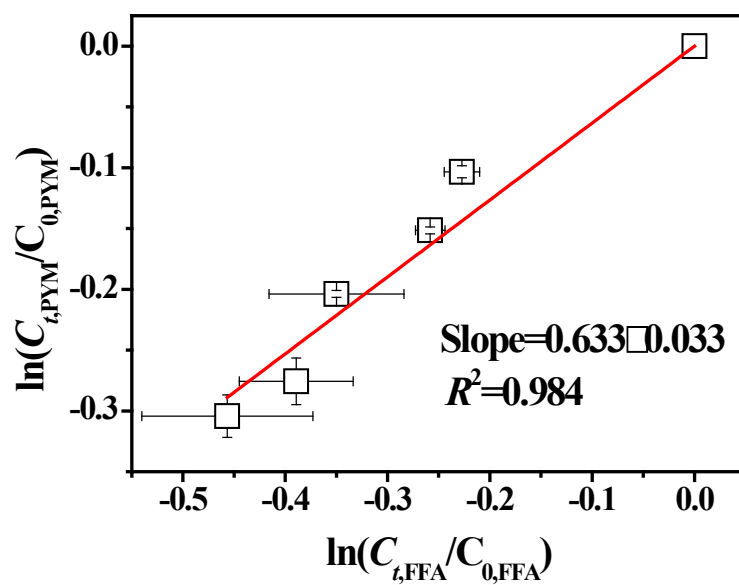Figure S6. Absorbance spectra of 2.5 μM tricyclazole (TC) and pymetrozine (PYM)

Figure S7. Competitive $^1O_2$ degradation of 800 μM furfuryl alcohol (FFA) and 10 μM PYM in 40 μM RB solution. $k_{^1O_2,PYM}$ values was determined by multiplying the slope (0.633) obtained from the plot by $k_{^1O_2,FFA}$ (1.00×10^8 M^{-1} s^{-1})
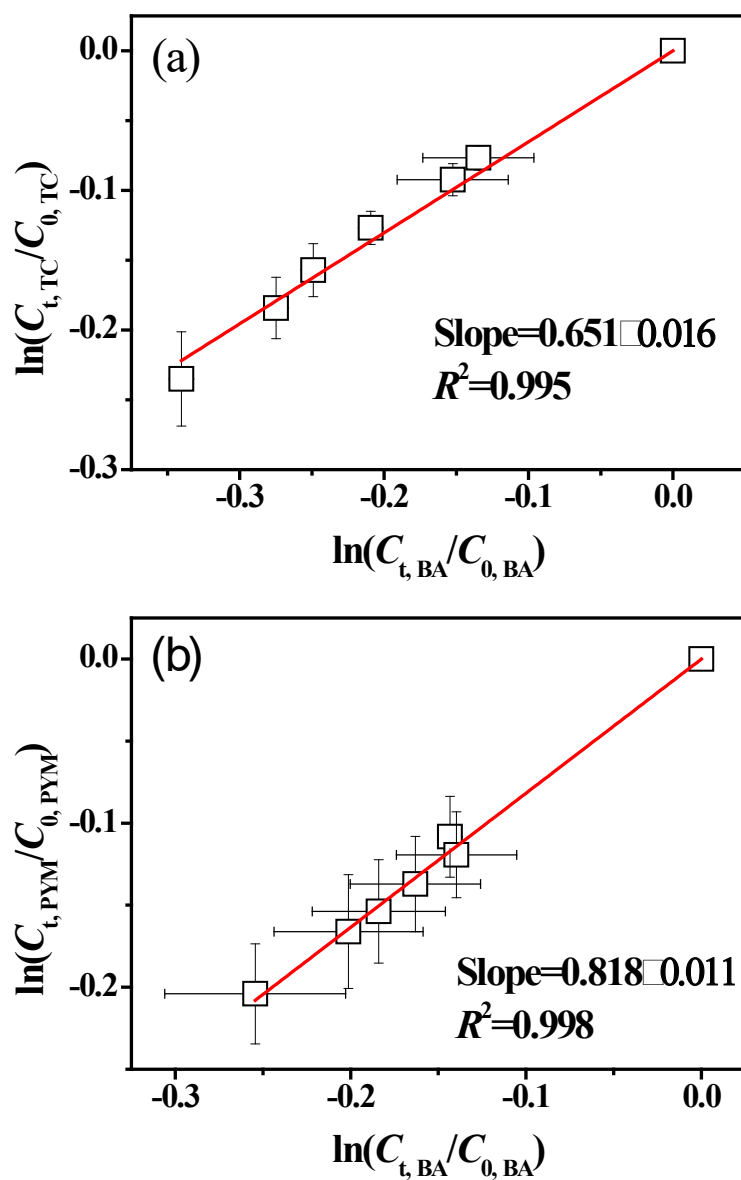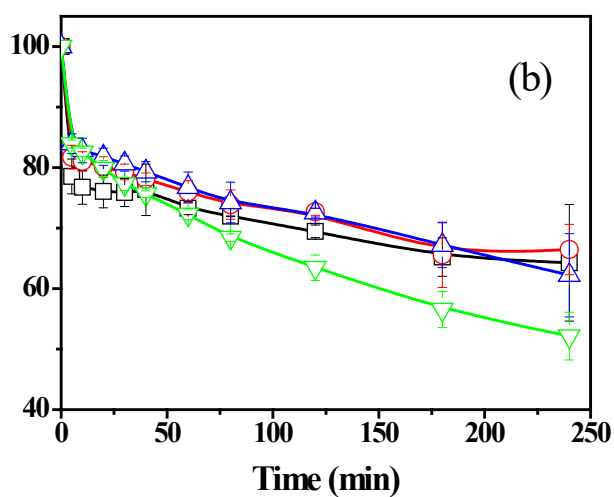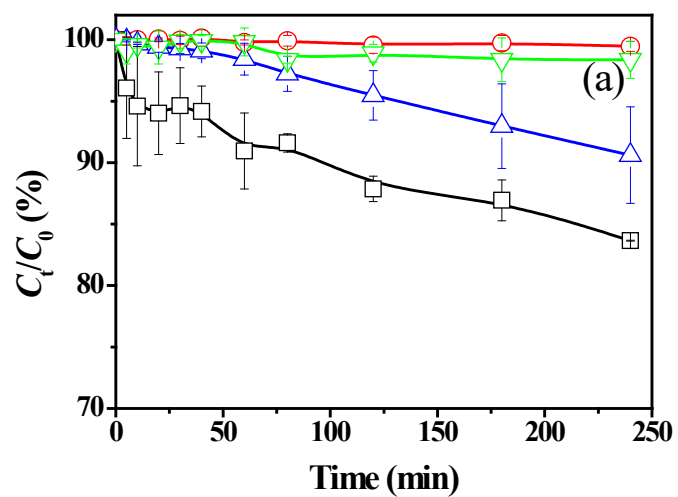
Figure S8. Competitive HO$^{\bullet}$ degradation of (a) benzoic acid (BA) and TC, (b) BA and PYM in Fenton solution ([H_2O_2]=300 μM, [Fe^{2+}]=33 μM). The $k_{HO^{\bullet},pesticide}$ values were determined by multiplying the slope obtained from these plots by $k_{HO^{\bullet},BA}$ (5.9×10^9 M^{-1} s^{-1}).

Figure S9. Photodegradation of 2.5 μM (a) TC and (b) PYM in RF1 water with and without
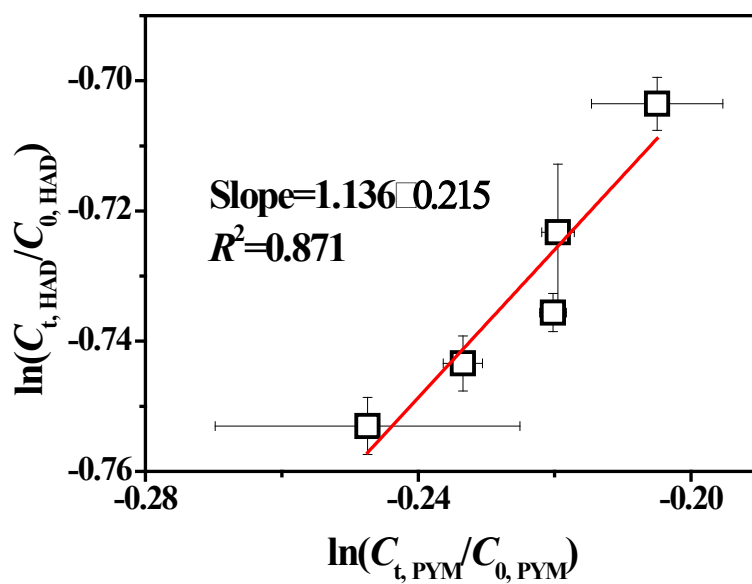
different scavengers

Figure S10. Competitive HO• degradation of 40 μM PYM and 20 μM HAD in Fenton solution ([H$_2$O$_2$]=300 μM, [Fe^{2+}]=33 μM). The $k_{\mathrm{HO•,HAD}}$ values were determined by multiplying the slope by the $k_{\mathrm{HO•,PYM}}$ (4.83×10^9 M^{-1} s^{-1})

Table S1. Basic information for 8 sampling sites in the Ganfu Plain Irrigation Area

Location	Descriptions of the sampling site
RF1	Rice at transplanting stage with height ~30 cm, located in Gaotian village
RF2	Rice at stooling stage with height ~75 cm, located in Gaotian village
RF3	Rice at stooling stage with height ~75 cm, located in Gaotian village
C1	Upstream of the irrigation canal
C2	Middle of the irrigation canal, located in Gaotian village
C3	Downstream of the irrigation canal, located in Youlan town
R1	Upstream of Fu River
R2	Downstream of Fu River

Table S2. Experimental conditions for the three-level two-factorial central composite design with a total of 13 runs

Runs	Design	
	T (°C)	Irradiation time (h)
1	9.8	7.05
2	40.0	12.00
3	27.5	7.05
4	27.5	7.05
5	15.0	2.10
6	27.5	7.05
7	27.5	7.05
8	27.5	0.05
9	27.5	7.05
10	27.5	14.05
11	45.2	7.05
12	15.0	12.00
13	40.0	2.10

Table S3. Additional data for physicochemical properties of surface water

Sample	RF1	RF2	RF3	C1	C2	C3	R1	R2
pH	6.48	6.77	6.73	8.83	6.85	6.95	7.66	7.15
Hardness ($CaCO_3$, mg/L)	52.9	20.6	19.6	23.5	22.5	27.5	23.5	27.5
Br^- (mg/L)	ND	ND	ND	ND	ND	ND	ND	ND
PO_4^{3-} (mg/L)	ND	ND	ND	ND	ND	ND	ND	ND
SO_4^{2-} (mg/L)	5.31	5.14	5.09	5.43	5.24	4.93	5.35	0.03
$Abs_{290-700nm}$	11.62	3.19	3.51	2.59	2.77	2.59	2.10	2.65

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