10.1071/EN24042
Environmental Chemistry

Supplementary Material

Photolysis characteristics and influencing factors of the pesticide pyrimethanil in natural waters

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Analysis of PYR products

A sample solution (20 mL) after irradiation was spiked with 1 μL of 2-hydroxy-5-chlorobiphenyl (100 μg L^{-1}) as the internal standard, and then was acidified to pH ~2 using 2.5 M H_2SO_4, followed by extraction with dichloromethane (10 mL, 2×). After dehydration using an anhydrous sodium sulfate column, the extract was concentrated to 1 mL for direct analysis by GC–MS. Analysis was performed using an Agilent 7890 GC and 5975C MSD with an EI source operating in SCAN mode. The GC was operated with helium as the carrier gas in the splitless mode with a DB-17ms capillary column (30 m × 0.25 mm × 0.25 μm). The following conditions were used for the analysis: a 1-μL injection, a source temperature of 230°C and an inlet temperature of 270°C. The column temperature ramp was as follows: 60°C for 2.0 min, 60–280°C at 20°C min^{-1} and 280°C hold 5 min.

Fluorescence spectra

Fluorescence spectra of the HA and SRNOM were obtained with an excitation at 350 nm and emission spectra between 360 and 600 nm. Excitation–emission matrix (EEM) spectrum of HA was obtained by continuous scanning of the emission wavelength from 250 to 650 nm by increasing the excitation wavelength from 200 to 550 nm. The EEM spectrum of SRNOM was obtained from IHSS.

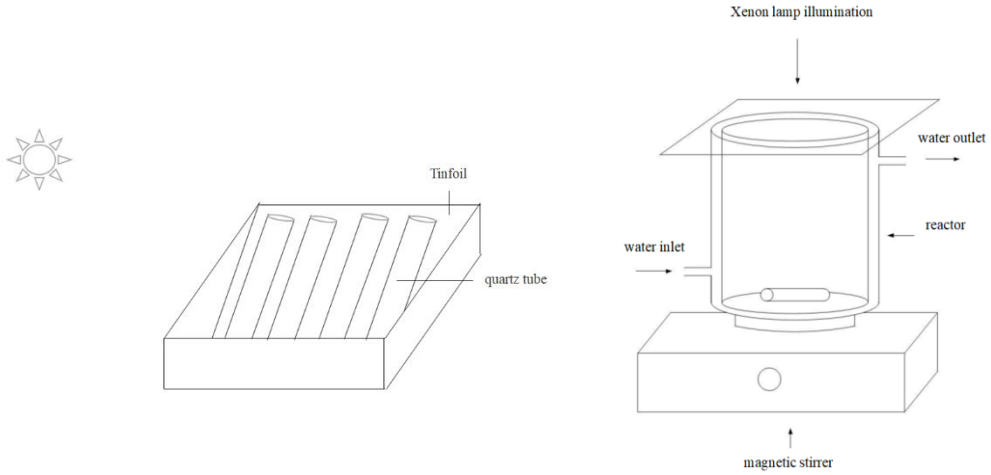


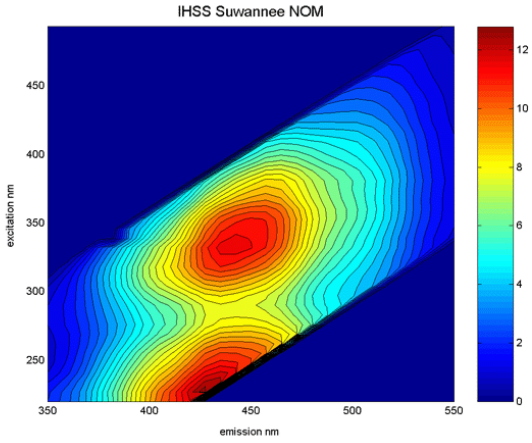
Fig. S1. Schematic diagram of the photochemical reactors for natural solar light irradiation (a) and enhanced artificial light irradiation (b).

Table S1. The photodegradation rate constants, R^2 and $t_{1/2}$ of PYR in pure water and natural waters under solar light irradiation

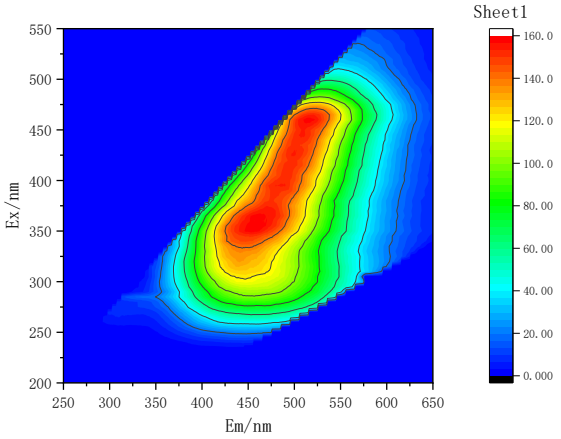
PYR (C_0 =5 mg L^{-1})	k (×10^3 h^{-1})	R^2	$t_{1/2}$ (h)
pure water	4.10±0.19	0.988	169±8.1
fresh water	14.4±2.5	0.868	49.6±8.6
after 12 h	8.37±0.51	0.985	83.1±5.2
seawater	12.0±0.86	0.975	57.8±4.1

Table S2. Element composition (%) of HA and SRNOM

	C	H	O	N
HA	42.92	3.01	51.83	0.90
SRNOM	50.70	3.97	41.48	1.27



SRNOM



HA

Fig S2. EEM spectra of SRNOM and HA.

Table S3. The photodegradation rates of PYR in the present of HA and SRNOM with or without Cl^- under the enhanced artificial light irradiation

PYR (C_0 =5 mg L^{-1})	k（h^{-1}）
In pure water	0.024±0.0028
In the presence of:	
0.43 mg of C per 1 L of HA	0.084± 0.0015
0.86 mg of C per 1 L of HA	0.114± 0.0030
2.15 mg of C per 1 L of HA	0.136±0.0055
4.29 mg of C per 1 L of HA	0.204±0.085
2.15 mg of C per 1 L of HA and 0.5 M NaCl	0.146 ± 0.0078
0.51 mg of C per 1 L of SRNOM	0.066±0.0094
1.01 mg of C per 1 L of SRNOM	0.084±0.0083
2.53 mg of C per 1 L of SRNOM	0.138±0.011
5.07 mg of C per 1 L of SRNOM	0.150±0.0074
2.53 mg of C per 1 L of SRNOM and 0.5 M NaCl	0.079±0.0067

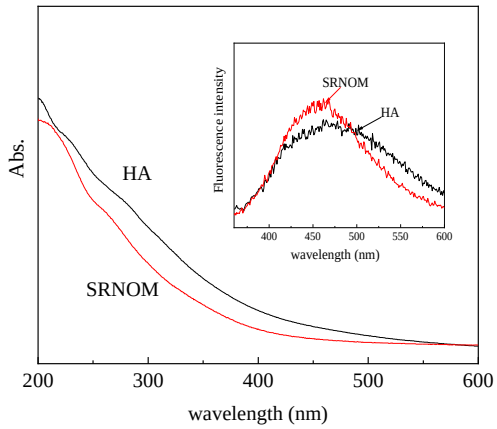
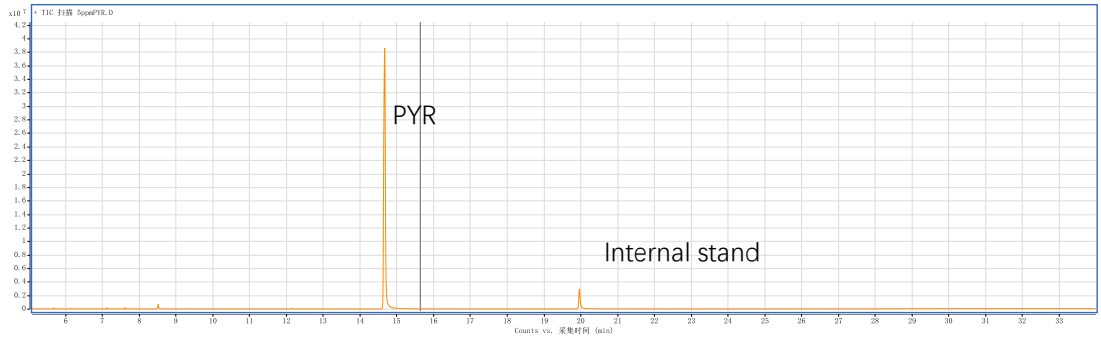
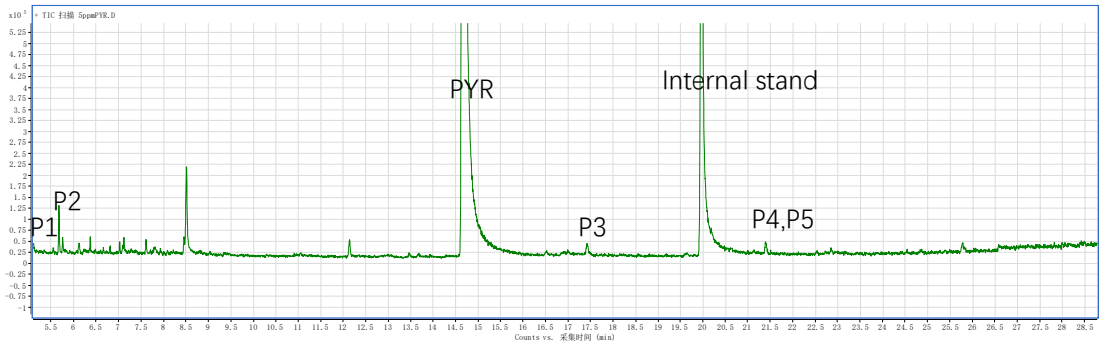


Fig S3. UV-Vis absorbance and fluorescence spectra of HA and SRNOM with excitation at 350 nm.

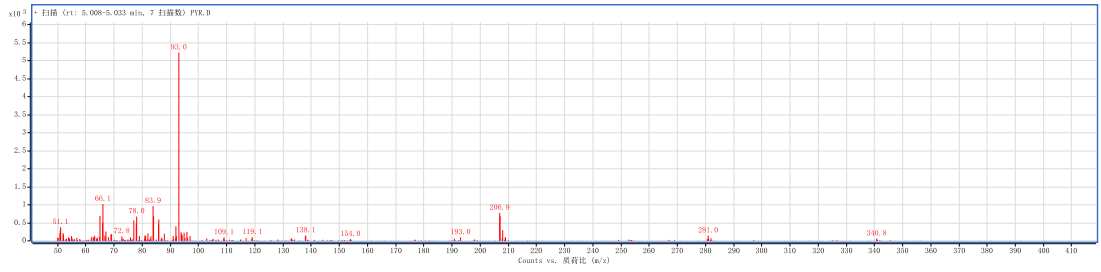
TIC



local magnification chromatogram

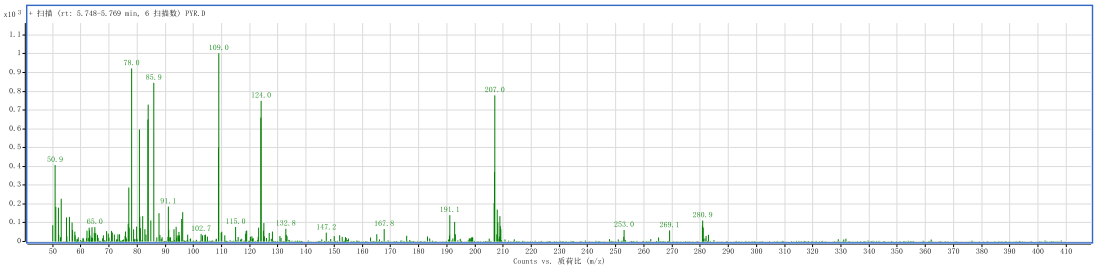


MS spectrum at 5.012min corresponding to P1

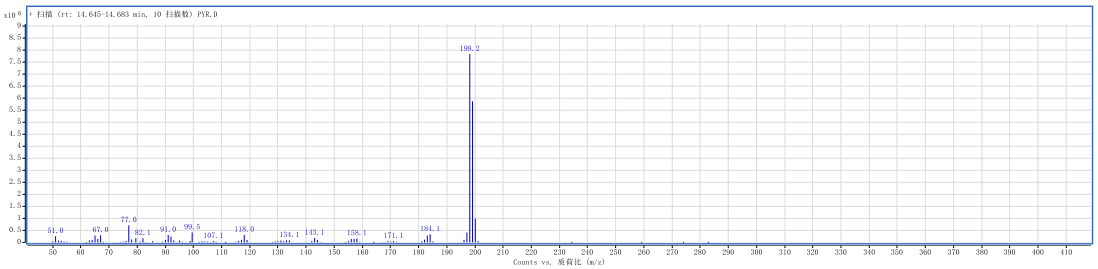


MS spectrum at 5.752min corresponding to P2

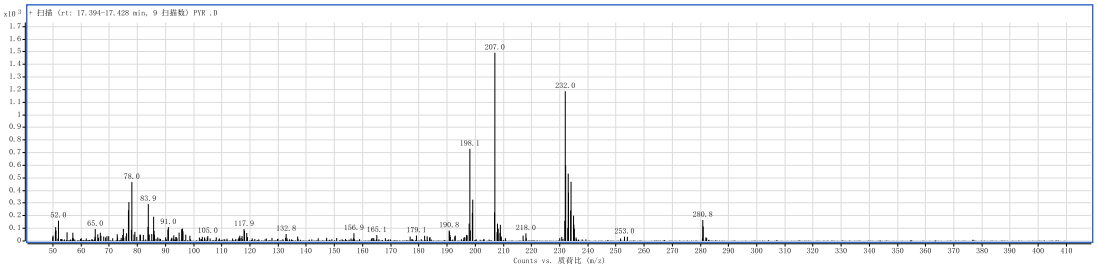
Fig. S4. Chromatograph and mass spectra of PYR and its photodegradation products



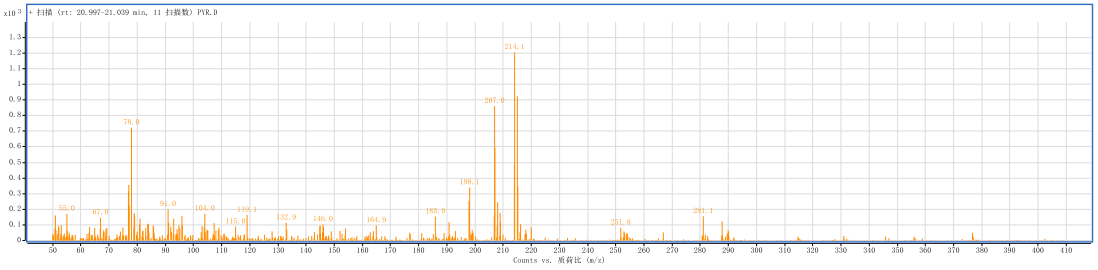
MS spectrum at 14.675min corresponding to PYR



MS spectrum at 17.398min corresponding to P3



MS spectrum at 21.001min and 21.327min corresponding to P4 and P5



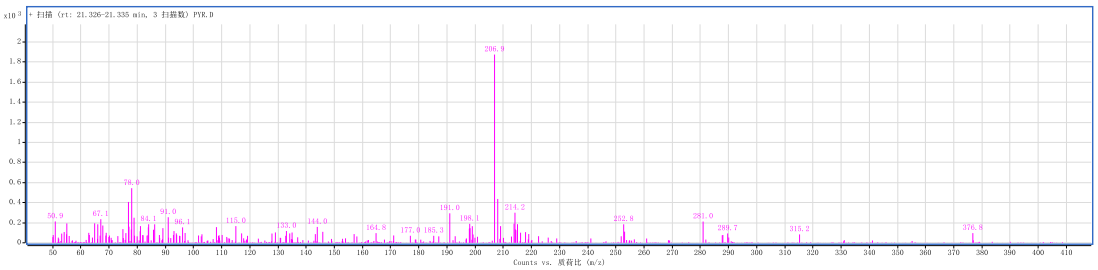
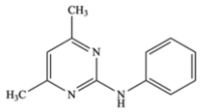
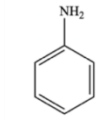
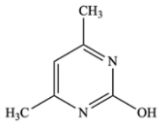
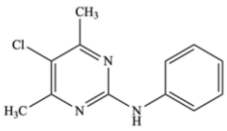
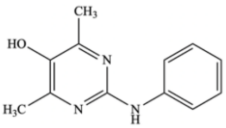
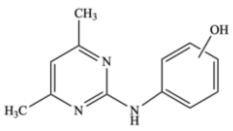


Fig. S4. (*Cont.*)

Table S4. Molecular structure information of PYR and its photodegradation products determined by GC-MS

	Structure of product	MW	Retention time (min)	Characteristic fragment ion (*m*/*z*)
Pyrimethanil		199	14.675	77, 82, 198
P1		93	5.012	77, 93
P2		124	5.752	78,109,124
P3		233	17.398	77,198,232
P4		215	21.001	78,198,214
P5		215	21.327	78, 198, 214