

Supplementary Information for

**Study on the Simulated Sunlight Photolysis Mechanism of Ketoprofen: Role of
Superoxide Anion Radical, Transformation Byproducts, and Ecotoxicity
Assessment**

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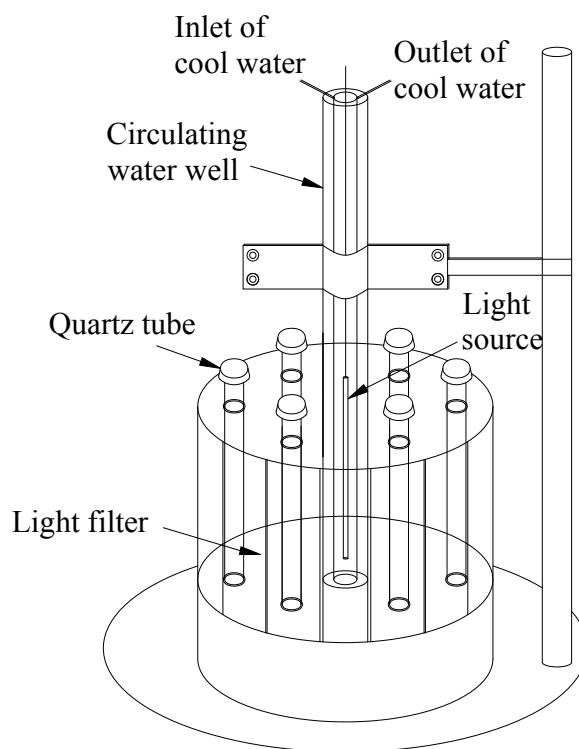


Fig. S1 Rotary photochemical reactor.

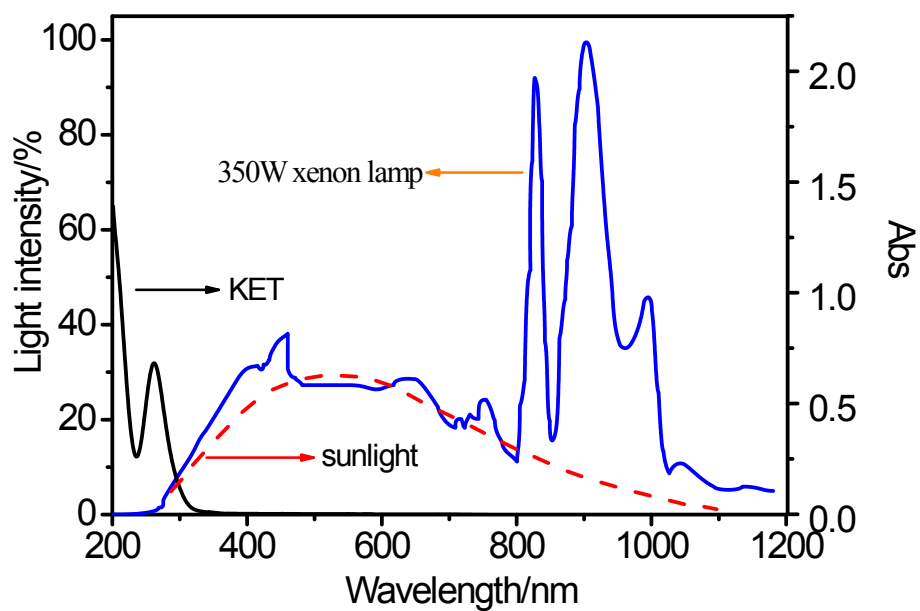


Fig. S2 Spectral energy distribution of xenon lamp and sunlight and the UV-visible absorption spectra of KET.

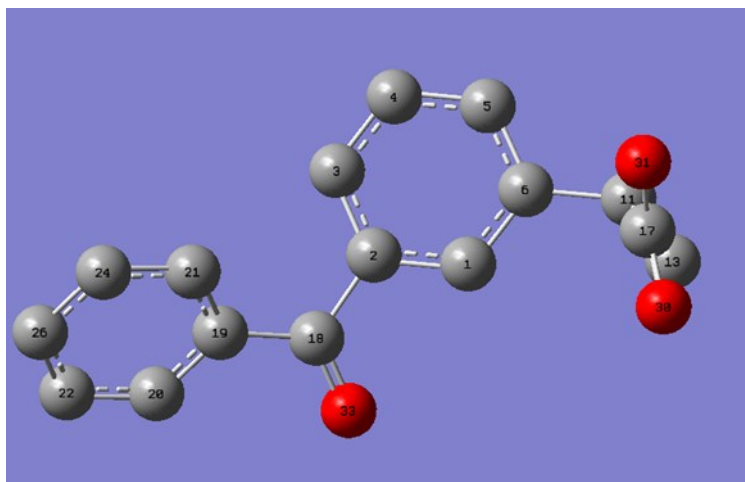


Fig.S3 The array of atoms model and atom number of KET.

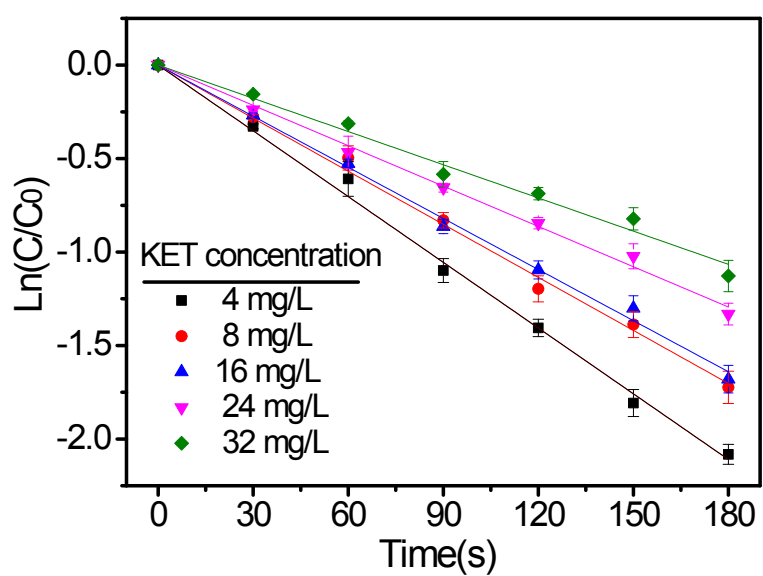


Fig.S4 Photodegradation kinetics of KET under different concentration.

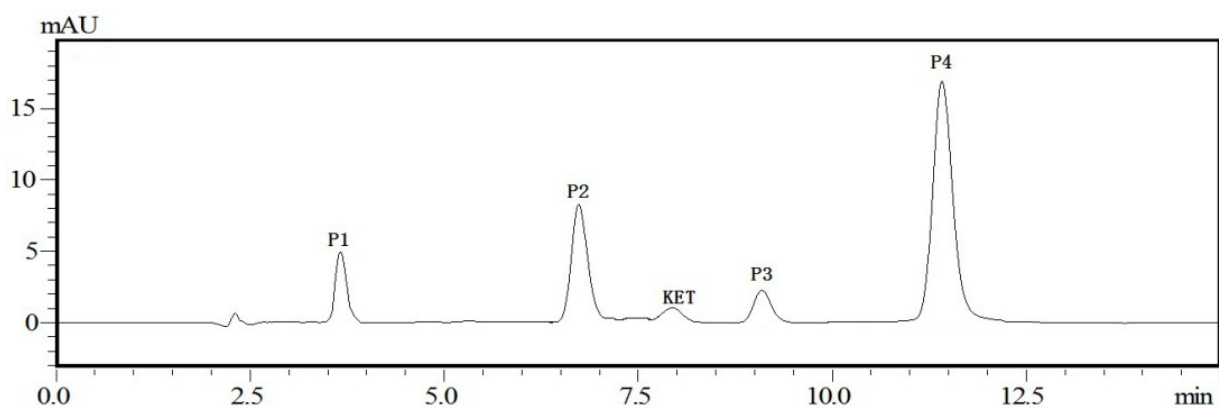


Fig. S5 HPLC-MS/MS total ion chromatogram of KET photoproducts under simulated sunlight irradiation.

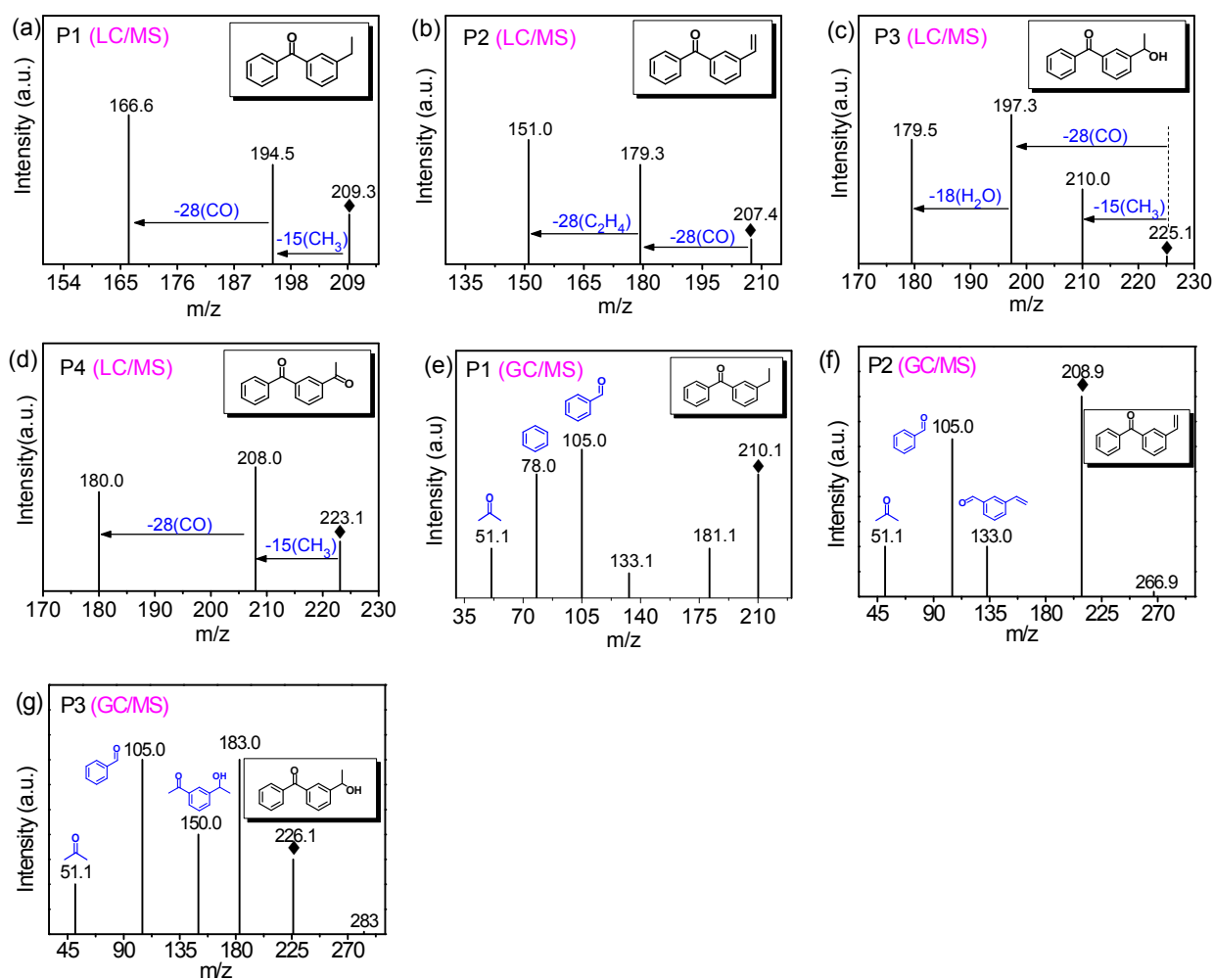


Fig. S6 Fragment chart analyses of the secondary ion mass spectrometry of KET byproduct by HPLC/MS/MS (a, b, c, and d) and by GC/MS (e, f, and g).

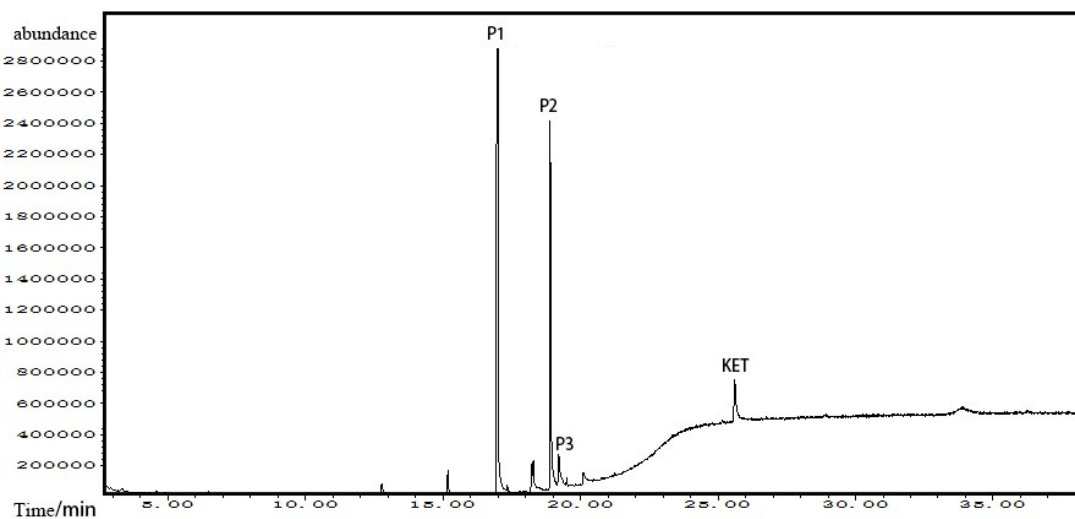


Fig. S7 GC total ion chromatogram of KET byproducts under simulated sunlight irradiation.

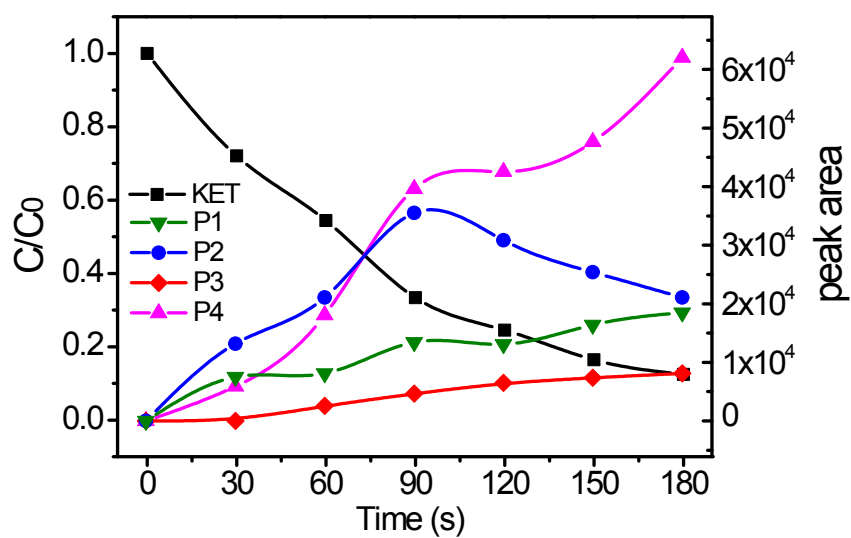


Fig.S8 The change of P1-P4 peak areas during the photolysis.

Tab. S1 Physical and chemical properties of KET.

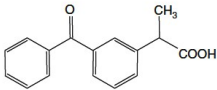
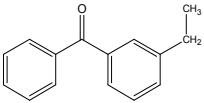
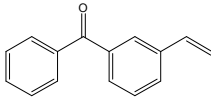
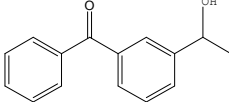
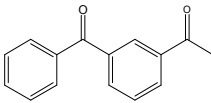
Drug	CAS	Chemical structure	MW	pK _a
ketoprofen	22071-15-4		254.2806	4.55

Table S2 River water chemical characterization.

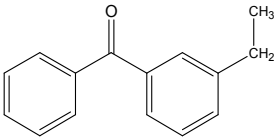
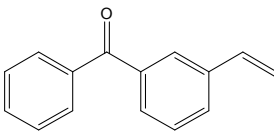
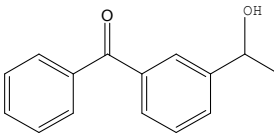
Parameter	Zhujiang River	Unit
	water	
pH	7.08	-
Uv ₄₀₀	0.0052	-
TOC	2.796	mg·L ⁻¹
Na ⁺	15.65	ppm
K ⁺	4.40	ppm
Ca ²⁺	28.03	ppm
Cl ⁻	15.61	ppm
SO ₄ ²⁻	27.25	ppm
HCO ₃ ⁻	297.1	ppm

Tab. S3 Mass spectrometry information and proposed structure of KET degradation products.

Peak	Retention	MW	Precursor	Fragments of MS ₂	Proposed structure
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	Time(min)	Ion(m/z)		(m/z)	
P1	3.661	210	209	194,171,156	
P2	6.787	208	207	179,151	
P3	9.081	226	225	210,207,197,179	
P4	11.568	224	223	208,195,180	

Tab. S4 Compounds identified by GC/MS during the photocatalytic degradation of KET under simulated sunlight irradiation.

Products	Retention Time(min)	MW	Fragments of MS ₂ (m/z)	Supposed structure
P1	16.9	210	51,78,105,210	
P2	18.8	208	51,105,133,208	
P3	19.5	226	51,105,147, 26	

Tab. S5 The bond dissociation energies (BDE) of KET.

Bond	C11-C17	C18-O33
Bond dissociation energies (au.)	0.1476	0.5114

Table S6 Evolution of acute and chronic toxicities of the degradation products of KET (mg·L⁻¹).

Products	Fish	Daphnid	Green Algee	Fish	Daphnid	Green Algee
	(LC ₅₀)	(LC ₅₀)	(LC ₅₀)	(Chv)	(Chv)	(Chv)
KET	591.752	354.567	329.895	61.630	40.161	97.385
P1	1.082	1.307	2.243	0.233	0.224	0.921
P2	2.471	1.695	2.761	0.302	0.280	1.102
P3	18.443	15.404	8.632	1.878	3.022	5.186
P4	33.266	20.389	20.831	3.558	2.460	6.467