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1           Aqueous photodegradation of the benzophenone fungicide  
2           metrafenone: Carbon-bromine bond cleavage mechanism

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## 22 **Abstract**

23 Metrafenone (MF), as a new type of benzophenone fungicide, has been widely  
24 used in agriculture and is persistent in the environment. Understanding its  
25 photochemical fate is essential for the comprehensive evaluation of its ecological risk.  
26 In the present work, we reported a detailed study on the photochemical transformation  
27 of MF in aqueous solution under irradiation (at  $\lambda > 290$  nm using a high pressure  
28 mercury lamp). MF was relatively photo-reactive showing a low polychromatic  
29 quantum yield of photolysis ( $1.06 \times 10^{-4}$ ) counterbalanced by a significant light  
30 absorption above 290 nm. A series of photoproducts were identified by high  
31 resolution mass spectrometry (HR-MS) analysis, and three different pathways,  
32 including oxidation of the methyl group, debromination and replacement of bromine  
33 by hydroxyl group were proposed. Among them, debromination was identified as the  
34 dominating process that could be achieved *via* homolytic C-Br bond cleavage from  
35 singlet and triplet MF, as confirmed by laser flash photolysis (LFP) experiments and  
36 density functional theory (DFT) calculations. Toxicity assessment revealed that  
37 photochemical degradation reduced the ecotoxicity of MF efficiently. Nitrate ions and  
38 humic acid promoted the MF photolysis, while bicarbonate exhibited no effect.  
39 Results obtained in this work would increase our understanding on the environmental  
40 fate of MF in sunlit surface waters.

41 **Keywords:** Metrafenone; Photolysis; Debromination; Homolytic cleavage; Bond  
42 dissociation energy.

## 43 **1. Introduction**

44 Fungicides are widely applied to control fungal pathogens on growing crops to  
45 improve yields (Cintia et al., 2021; Lin et al., 2020; Miller et al., 2021; Nermine et al.,  
46 2021; Patrick et al., 2021; Regueiro et al., 2015). Metrafenone (MF) is a new type of

47 benzophenone derivative fungicide, which is a brand-new active ingredient in the  
48 field of phytochemical protection (structure in Fig. 1). Studies have demonstrated that  
49 MF is effective in reducing spore germination, preventing appressorium formation,  
50 and inhibiting powdery mildew infestation (Franck et al., 2000; Krystina et al., 2006).  
51 Hence, it has been widely used to prevent and treat powdery mildew in crops such as  
52 wheat and grapes. However, repeated application of fungicides over a longtime period  
53 would inevitably lead to their accumulation in the environment. These toxic  
54 compounds can leach out of the soil, and contaminate surface water and groundwater,  
55 inducing potential health risks to residents (Freya and Jane, 2004; Pimmata et al.,  
56 2013). In agricultural production, MF is normally pre-applied and there is a tendency  
57 to increase the amount applied as microbial resistance increases, resulting in its  
58 persistence in the environment (Kunova et al., 2016; Leroux et al., 2013). Residual  
59 MF has been widely detected in grapes, juices, and wines after its application to vines,  
60 which eventually affect the human health (Briz-Cid et al., 2014; Cabras and Angioni,  
61 2000; Noelia et al., 2018; Noguerol et al., 2010). Regueiro et al. (2015) once  
62 evaluated the toxicity of MF on cortical neurons in mice, they reported that MF  
63 induces depolarization of mitochondrial membranes, reduces cellular activity, and  
64 exhibits toxic effects after 7 days of exposure (Regueiro et al., 2015).

65 **Fig. 1.**

66 In order to accurately assess the ecological risks of fungicides, it is essential to  
67 investigate their transformation and fate in the environment (Baćmaga et al., 2019).  
68 Photochemical transformation is among the most important processes that affect the

69 fate of organic compounds in surface water (Ge et al., 2009; Yong et al., 2009). Direct  
70 photolysis of fungicides is caused by direct absorption of photons, while indirect  
71 photolysis is triggered by the absorption of light by photosensitizers. Active  
72 components in water (such as dissolved organic matter and ions) can interact with  
73 organic pollutants through energy transfer of excited substances or through  
74 photoproduction of reactive transient species, which affects the persistence and fate of  
75 fungicides in the environment (Avetta et al., 2014; Fréneau et al., 2019; Jennifer et al.,  
76 2019; Liu et al., 2016). As shown in Fig. 1, the molecular structure of MF contains  
77 chromophores such as benzene rings and carbonyl groups which can absorb  
78 ultraviolet or visible light, indicating that direct photolysis of MF is likely upon  
79 irradiation (Turro, 1978). López-Fernández et al. (2018) confirmed that photolysis is  
80 an effective route for the removal of MF from grape juice (López-Fernández et al.,  
81 2018). However, to our knowledge, specific studies on the photolytic fate of MF in  
82 natural surface waters is quite limited.

83 In the current study, the photolytic behavior of MF in aqueous solution is  
84 investigated systematically, the main degradation pathways and mechanisms are  
85 proposed. For this, steady-state irradiations are performed to measure the quantum  
86 yield of MF photolysis, the second order rate constant ( $k_{^1\text{O}_2,\text{MF}}$ ) for the reaction  
87 between singlet oxygen ( $^1\text{O}_2$ ) and MF and test the effect of pH and quenchers. In  
88 addition, laser flash photolysis (LFP) experiments are conducted to identify the  
89 transient species involved in the reaction and density functional theory (DFT)  
90 calculations are adopted to confirm the hypotheses. The and MF and are also

91 measured. The photodegradation products of MF are determined by high resolution  
92 mass spectrometry (HR-MS) and their toxicity is evaluated by Ecological Structure  
93 Activity Relationship (ECOSAR 2.0) software. Subsequently, the effects of water  
94 matrices including nitrate ions, bicarbonate, and humic acid on MF photodegradation  
95 are evaluated. Results obtained here will provide a scientific basis for a  
96 comprehensive understanding of the photochemical fate of MF in the aquatic  
97 environment.

## 98 **2. Materials and methods**

### 99 *2.1. Materials*

100 Metrafenone (MF, 99.7%) and humic acid (HA, 99%) were purchased from  
101 Sigma-Aldrich (St. Louis, MO, USA). Phosphoric acid with chromatographic purity  
102 and sorbic acid (99.8%) were obtained from Aladdin (Shanghai, China). Deuterium  
103 oxide (D<sub>2</sub>O, 99.9%) was obtained from Energy Chemical (Shanghai, China).  
104 Isopropanol (IPA, 99.9%) was obtained from Thermo Fisher Scientific (Waltham,  
105 USA). Sodium nitrate (≥98.5%) and sodium bicarbonate (≥99.5%) were purchased  
106 from Sinopharm Chemical Reagent Co., Ltd and Richjoint, respectively. HPLC grade  
107 acetonitrile (ACN, 99%) was obtained from J&K Scientific Ltd (Shanghai, China).  
108 Other reagents were at least of analytical grade and used as received.

### 109 *2.2. Photolysis experiments*

#### 110 *2.2.1 Steady-state photolysis experiments*

111 Steady-state photolysis experiments were conducted in a device equipped with a  
112 500 W high pressure mercury lamp (Beijing Zhongjiao Jinyuan Technology Co., Ltd,

113 China) surrounded by a 290 nm cut-off filter as the light source. The mercury lamp  
114 was turned on preliminarily for 30 min. After stabilization, 25 mL solution to be  
115 irradiated containing target compounds (20  $\mu$ M) were pipetted into a Pyrex glass  
116 reactor. During the irradiation process, Pyrex glass reactors were transferred to the  
117 water-cooled immersion well in the device to maintain the temperature at 20  $^{\circ}$ C. Dark  
118 controls were also performed under the same conditions. During the irradiated process,  
119 0.5 mL aliquot of the solution to be irradiated was withdrawn at predetermined time  
120 intervals for analysis. To ensure the reliability of the data, all experiments were  
121 carried out at least in duplicates, and the error bars in the figures represent the  
122 standard deviation (SD).

### 123 *2.2.2 Laser flash photolysis experiments*

124 Laser flash photolysis (LFP) experiments were carried out using a Quanta Ray  
125 LAB-150–10 Nd:YAG laser at an excitation wavelength of 266 nm to investigate the  
126 absorbance and disappearance of the transient species in ACN solutions of MF.  
127 Solutions were purged with purified N<sub>2</sub> prior to the experiments to evaluate the effect  
128 of O<sub>2</sub> (triplet quencher) on the lifetime of transient species. Different time windows  
129 were used to fit the decay of the transient species of MF.

### 130 *2.3. Analytical methods*

131 The concentration of MF was measured using a high performance liquid  
132 chromatograph (HPLC, Waters) equipped with a separation module (Waters 2695)  
133 and a photodiode array detector (Waters 2998). Detailed operation conditions are  
134 provided in Text. S1.

135 The transformation products were identified by a high resolution mass  
136 spectrometry (HR-MS), which was coupled to a HPLC Waters Alliance system for  
137 chemical separation. The details of HR-MS analysis are given in Text. S2.

138 The bromine ion concentration was measured by ion chromatograph and the  
139 details are provided in Text. S3.

140 The details for electron paramagnetic resonance spectroscopy analysis (EPR) are  
141 illustrated in Text. S4.

#### 142 *2.4 Quantum yield*

143 The polychromatic quantum yields of MF ( $\Phi_{MF}$ ) direct photolysis in aqueous  
144 solutions were determined using *p*-nitroanisole (PNA)/pyridine (pyr) as an  
145 actinometer according to Eq. (1).

$$146 \quad \Phi_{MF} = \frac{k_{MF}}{k_{PNA}} \times \frac{\sum_{\lambda} (L_{\lambda} \epsilon_{\lambda, MF})}{\sum_{\lambda} (L_{\lambda} \epsilon_{\lambda, PNA})} \times \Phi_{PNA} \quad (1)$$

147 where  $k_{MF}$  and  $k_{PNA}$  were the observed photolysis rate constant of MF and PNA,  
148 respectively.  $\epsilon_{\lambda}$  ( $\text{mol}^{-1} \text{cm}^{-1}$ ) represented the molar absorptivity and  $L_{\lambda}$  ( $\text{cm}^{-2} \text{s}^{-1}$ ) was  
149 the incident light intensity.  $\sum_{\lambda} (L_{\lambda} \epsilon_{\lambda, MF})$  and  $\sum_{\lambda} (L_{\lambda} \epsilon_{\lambda, PNA})$  were the light absorption  
150 for MF and actinometer, respectively.  $\Phi_{PNA}$  was the quantum yield of PNA and was  
151 calculated according to  $\Phi_{PNA} = 0.29[\text{pyr}] + 0.00029$  (Laszakovits et al., 2016). The  $\epsilon_{\lambda}$   
152 values of aqueous MF and PNA solutions were measured using a UV-Vis  
153 spectrophotometer and specific pathlength quartz cells.

#### 154 *2.5. DFT calculations*

155 In this study all the density functional theory (DFT) calculations were conducted  
156 by using Gaussian 16 package with hybrid density functional B3LYP method. The



157 details for DFT calculation were illustrated in Text. S6.

## 158 *2.6. Ecotoxicity assessment*

159 The aquatic toxicity data was an essential judgment basis for environmental  
160 hazard classification and ecological risk assessment of chemicals (Cash, 1998). In the  
161 present study, the ecotoxicity of MF and photoproducts was evaluated by the  
162 Ecological Structure Activity Relationship (ECOSAR 2.0). Three classical aquatic  
163 organisms (green algae, daphnia and fish) were assessed for acute toxicity (half-lethal  
164 and half-effect concentration (LC50, EC50)) and chronic toxicity values (Chv) (Wang  
165 et al., 2019).

## 166 **3. Results and discussion**

### 167 *3.1 Direct photolysis of MF*

168 The UV-Vis absorption spectrum of aqueous MF exhibits a broad absorption  
169 band ranging from 260 to 350 nm ( $\lambda_{\max} = 292$  nm,  $\epsilon_{292} = 7750$  mol<sup>-1</sup> cm<sup>-1</sup>) thus well  
170 overlapping with the emission spectrum of the mercury lamp (Fig. 2) and of the solar  
171 spectrum, implying that direct photodegradation can potentially take place for MF in  
172 natural conditions. The absorption band of MF is mainly due to the presence of  
173 chromophores such as benzene and ketone groups that are capable of absorbing  
174 UV-Vis light. In the present study, the absorption band corresponds to the low energy  
175  $\pi \rightarrow \pi^*$  excitation due to the presence of the benzene chromophore rather than the  
176 ketone chromophore ( $n \rightarrow \pi^*$  excitation) (Turro, 1978). This could be further  
177 confirmed by TD-DFT calculations, as shown in Fig. S1, the broad band ranging from  
178 260 nm to 350 nm is attributed to the S1 to S5 absorptions, among which the S4 state

179 has the largest oscillator strength (Table. S1). We thus analyzed the molecular orbital  
180 (MO) transition contributions of the S4 state. The two main transitions are the highest  
181 occupied molecular orbital (HOMO)-2 to the lowest unoccupied molecular orbital  
182 (LUMO) and HOMO-1 to LUMO. Based on the isosurfaces of HOMO-2 ( $\pi$ ),  
183 HOMO-1 ( $\pi$ ), and LUMO ( $\pi^*$ ) (Fig. S2), the excitation can be assigned to a  $\pi \rightarrow \pi^*$   
184 transition. In addition, solvatochromic experiments by using ACN as a solvent could  
185 also demonstrate this phenomenon of absorption band distribution (Fig. 2). Molecules  
186 that undergo a  $\pi \rightarrow \pi^*$  transition are believed to have excited states more strongly  
187 polarized than the ground state. Therefore, a strongly polar solvent (such as water) has  
188 a greater stabilizing effect on the excited state and can reduce the energy difference  
189 between the excited state and the ground state. Therefore, as polarity of the solvent  
190 decreased with the solvent substitution of H<sub>2</sub>O by ACN, the absorption was  
191 hypochromatically shifted, which implied that the energy required from the ground  
192 state to the excited state became larger, demonstrating that the MF molecule  
193 underwent a  $\pi \rightarrow \pi^*$  transition (Da et al., 2001). The  $n \rightarrow \pi^*$  excitation was not  
194 observed (or was weak) because of the poor spatial overlap of the n and  $\pi^*$  orbitals,  
195 resulting in a weak vibronic intensity, which should theoretically be at 350 nm (Lim  
196 and Jack, 1966).

197 **Fig. 2.**

198 Dark control experiments showed no loss of MF, therefore, hydrolytic or  
199 microbial degradations were not further considered in this study. Upon irradiation, a  
200 significant MF decay was observed, implying that photolysis limited the persistence

201 of MF in aqueous solutions. The decay of MF could be fitted by a pseudo-first-order  
202 kinetics, and the observed rate constant ( $k_{\text{obs}}$ ) was calculated by linear regression of  
203 logarithmic concentration values ( $\ln([\text{MF}]_t / [\text{MF}]_0)$ ) determined as a function of time  
204 (Eq. (2)). Half-life ( $t_{1/2}$ ) was also calculated according to Eq. (3). In the present work,  
205  $k_{\text{obs}}$  was determined to be  $0.056 \pm 0.003 \text{ h}^{-1}$  under simulated sunlight, corresponding  
206 to a half-life ( $t_{1/2}$ ) of  $12.4 \pm 0.6 \text{ h}$ . These values were comparable with that reported  
207 values ( $0.072 \pm 0.005 \text{ h}^{-1}$  ( $k_{\text{obs}}$ ) and  $9.6 \pm 0.7 \text{ h}$  ( $t_{1/2}$ )) (López-Fernández et al., 2018).  
208 European Food Safety Authority (EFSA) concluded that the half-life of MF in the  
209 dark aerobic water sediment system (biological degradation) is 8.5-9.2 days (EFSA.,  
210 2006). It clearly shows that MF is difficult to biodegrade, therefore, we can conclude  
211 that photolysis plays an important role in the elimination of MF in the aquatic  
212 environment.

$$213 \quad \ln([\text{MF}]_t / [\text{MF}]_0) = -k_{\text{obs}}t \quad (2)$$

$$214 \quad t_{1/2} = \ln 2 / k_{\text{obs}} \quad (3)$$

215 Quantum yields are important parameters in photochemistry. The quantum of a  
216 given process or of a global reaction corresponds to the ratio of photons triggering a  
217 photochemical process or the reaction to the total number of absorbed photons (Rene,  
218 2002) and therefore gives the efficiency of absorbed photons to achieved the process  
219 or the reaction. Here, the polychromatic quantum yield of MF photolysis ( $\Phi_{\text{MF}}$ ) at 20  
220  $\mu\text{M}$  was determined to be  $1.06 \times 10^{-4}$ , which is higher than the quantum yields of  
221 photolysis of other benzophenone derivatives that do not contain halogene atoms such  
222 as benzophenone-3 ( $1.51 \times 10^{-5}$ ) and 4-hydroxy-benzophenone ( $7.91 \times 10^{-6}$ ) (Li et al.,

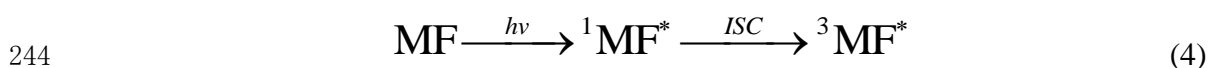
223 2016). This result suggests that the presence of a Br atom in MF may favor the  
224 photodegradation.

225 The potential impact of pH solution on MF photolysis was also tested. Our results  
226 indicated that the rate of photodegradation was barely affected by the solution pH  
227 between 4 and 10 (Fig. S4). This phenomenon is reasonable based on the  
228 pH-independent absorption spectra of MF (Fig. S5) and on the absence of dissociable  
229 functional groups in the molecular structure of MF.

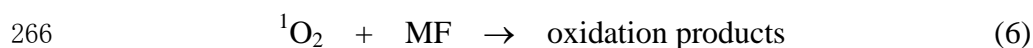
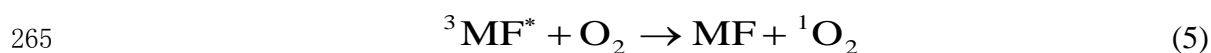
### 230 *3.2 Identification of potential reactive intermediates*

231 The triplet excited state of carbonyls has attracted a wide interest as a special  
232 oxidant in photochemical reactions. Upon irradiation, MF molecules were likely to  
233 absorb photons to make an energy level transition from the ground state to the singlet  
234 excited state ( $^1\text{MF}^*$ ), followed by an intersystem crossing (ISC) process to generate  
235 the triplet excited state ( $^3\text{MF}^*$  containing two electrons with the same spin direction  
236 and unpaired) (Eq. (4)) (Nicholas et al., 2012).

237 The presence of a bromine atom in MF molecule is expected to enhance the  
238 spin-orbit coupling due to the heavy halogen effect, thus favoring the ISC process.  
239 Therefore, the generation of  $^3\text{MF}^*$  and its involvement in the photolysis process is  
240 likely. Sorbic acid (a triplet excited state quencher) was added to the MF solution to  
241 test the involvement of  $^3\text{MF}^*$  (Zhou et al., 2013). As shown in Fig. 3, the presence of  
242 sorbic acid (0.4 mM) partially inhibited the reaction, confirming the involvement of  
243  $^3\text{MF}^*$  in the photo-transformation.



245 It has been reported that the energy required to excite many aromatic compounds to  
246 their triplet excited states was greater than 250 kJ mol<sup>-1</sup>, whereas the energy for <sup>1</sup>O<sub>2</sub>  
247 formation was only 94 kJ mol<sup>-1</sup> (Zepp et al., 1987). Therefore, under irradiation,  
248 energy transfer between the triplet excited state of organic compounds and dissolved  
249 oxygen may occur, resulting in the production of <sup>1</sup>O<sub>2</sub>. For example, the triplet excited  
250 state energy of benzophenone was as high as 288 kJ mol<sup>-1</sup>, which was sufficient to  
251 transfer energy to dissolved oxygen and generate <sup>1</sup>O<sub>2</sub> with a quantum yield of 0.34  
252 (Turro et al., 2012). Since replacing H<sub>2</sub>O with D<sub>2</sub>O extends the lifetime of <sup>1</sup>O<sub>2</sub> 13-fold  
253 (Rodgers and Snowden, 1982) a D<sub>2</sub>O-H<sub>2</sub>O mixture (50:50, v:v) was employed as a  
254 solvent to investigate whether <sup>1</sup>O<sub>2</sub> was produced in the reaction and was responsible  
255 for MF oxidation. The reaction rate constant increased by a factor of 1.64 when the  
256 solvent was changed to the mixture of D<sub>2</sub>O-H<sub>2</sub>O (Fig. 3), indicating that <sup>1</sup>O<sub>2</sub> was  
257 generated in the photolysis of MF by photosensitization. Therefore, these results are  
258 consistent with the formation of <sup>3</sup>MF\* and the generation of <sup>1</sup>O<sub>2</sub> by energy transfer to  
259 O<sub>2</sub> (Eq. (4) and (5)). Once formed, <sup>1</sup>O<sub>2</sub> could react with MF (Eq (6)). We therefore  
260 further measured the bimolecular rate constant of this reaction,  $k_{^1O_2, MF}$ . The value  
261 found: 5.6 × 10<sup>7</sup> L mol<sup>-1</sup> s<sup>-1</sup> demonstrated the easy oxidation of MF by <sup>1</sup>O<sub>2</sub>.  
262 Furthermore, the irradiation of MF in the presence of isopropanol (0, 8 and 20 mM)  
263 used as an •OH radical scavenger ruled out the involvement of this radical in the  
264 photolysis of MF (Fig. S6).



267

268

### Fig. 3.

269

270 In the case MF disappears through Eq (6), the rate of MF loss can be written:

$$271 \quad -d[\text{MF}]/dt = I_a \times \Phi_{\text{SO}} \times (k_{1\text{O}_2,\text{MF}} \cdot [\text{MF}] / (k_{1\text{O}_2,\text{MF}} \cdot [\text{MF}] + k_d) \quad (7)$$

272 Where  $I_a$  is the rate of light absorption by MF,  $\Phi_{\text{SO}}$ , the quantum yield of  $^1\text{O}_2$   
273 formation and  $k_d$ , the rate of  $^1\text{O}_2$  desactivation in water ( $2.5 \times 10^5 \text{ s}^{-1}$ , Rodgers and  
274 Snowden, 1982). Moreover,  $\Phi_{\text{MF}}$  is equal to :

$$275 \quad \Phi_{\text{MF}} = -d[\text{MF}]/dt/I_a = \Phi_{\text{SO}} \times (k_{1\text{O}_2,\text{MF}} \cdot [\text{MF}] / (k_{1\text{O}_2,\text{MF}} \cdot [\text{MF}] + k_d) \quad -(8)$$

276 It means that  $\Phi_{\text{MF}}$  depends on the  $[\text{MF}]$ , in particular when  $k_{1\text{O}_2,\text{MF}} \cdot [\text{MF}] \ll k_d$ , that is  
277 the case at the chosen concentrations. To check this, we measured  $\Phi_{\text{MF}}$  for several  
278 concentrations ranging from 20 to 5  $\mu\text{M}$ .  $\Phi_{\text{MF}}$  decreased from  $1.06 \times 10^{-4}$  for 20  $\mu\text{M}$  to  
279  $0.52 \times 10^{-4}$  for 5  $\mu\text{M}$ , in accordance with a contribution of  $^1\text{O}_2$  to the  
280 phototransformation of MF.

281

282 M. A. J. Rodgers, P. T. Snowden. Lifetime of ( $^1\text{O}_2$ ) in Liquid Water As Determined by  
283 Time-Resolved Infrared Luminescence Measurements. J. Am. Chem. Soc. 1982,  
284 104, 5541-5543. [doi-org.ezproxy.uca.fr/10.1021/ja00384a070](https://doi.org/10.1021/ja00384a070)

285

### 286 *3.3 Photoproducts identification*

287 In this work, we systematically investigated intermediate photoproducts of MF  
288 via HR-MS analysis after 22 h irradiation. The major intermediate photoproducts are

289 listed in Table. S2. Bromine atom has two isotopes (relative atomic mass 78.9183 and  
290 80.9163), based on this property, isotopic features were used as a diagnostic tool for  
291 the identification of photoproducts containing bromine atoms. For instance, the parent  
292 compound MF had a molecular ion cluster corresponding to  $m/z = 409.0634/411.0612$   
293 ( $[M+H]^+$ ) with retention time of 4.91 min, suggesting that the molecular structure of  
294 MF contained one bromine atom. Reviewing Table. S2, it can be seen that eight  
295 photoproduct intermediates were detected. Specifically, TP1 with  $m/z =$   
296  $423.0426/425.0404$  ( $[M+H]^+$ ) at retention time of 1.97/2.65 min was assigned as the  
297 oxidation product in which a methyl group was oxidized into aldehyde. The  $m/z =$   
298  $439.0375/441.0353$  ( $[M+H]^+$ ) molecular ion was labeled as the secondary product  
299 (TP2), which was generated by oxidation of the methyl group to carboxyl with  
300 retention time of 1.28/1.6 min. Based on the total ion currents (TICs), debrominated  
301 product (TP3) was a major intermediate product generated during MF photolysis (Fig.  
302 S7), which was eluted at 2.56 min with  $m/z = 331.1530$ . Furthermore,  
303 debrominated-methyl oxidation products (TP4 and TP5) were identified based on  $m/z$   
304  $= 345.1325$  and  $361.1273$  ( $[M+H]^+$ ) with retention time of 1.63/1.90 and 1.22/1.41  
305 min, respectively. Notably, TP3, TP4 and TP5 were also observed in a previous study  
306 (López-Fernández et al., 2018). Moreover, TP6 with  $m/z = 347.1480$  ( $[M+H]^+$ ) was  
307 identified as the OH substitution product, which was another major debromination  
308 product (Fig. S7). To the best of our knowledge, the formation of  
309 debrominated-hydroxylated photoproduct in the photolysis of MF was reported for the  
310 first time. TP7 and TP8 ( $m/z = 361.1273$  and  $377.1221$ ,  $[M+H]^+$ ) were assigned to the

311 methyl oxidized from of TP6.

312 To gain deeper insight into the debromination process, the evolution of releasing  
313 bromide was recorded during the photolysis of MF, and the yield of bromide was  
314 calculated according to Eq. (9) (Xu et al., 2020):

$$315 \quad \text{Yield of bromide} = \frac{[\text{Br}^-]_t}{[\text{MF}]_0 - [\text{MF}]_t} \times 100\% \quad (9)$$

316 where  $[\text{Br}^-]_t$  is the concentration of bromide ion detected at irradiation time  $t$ ;  $[\text{MF}]_0$   
317 and  $[\text{MF}]_t$  are the concentrations of MF at irradiation time zero and  $t$ , respectively.

318 Based on the results of ion chromatography, we obtained an average bromine yield of  
319  $73 \pm 1\%$  for MF direct photolysis (Fig. S8), which confirmed our conclusion that  
320 debromination is a major pathway in the direct photolysis of MF.

### 321 *3.4 Photolysis pathways*

322 Based on the detected intermediates, several photodegradation pathways of MF  
323 are proposed (Fig. 4). Pathway I corresponded to the oxidation of the  $\beta$ -methyl group,  
324 giving rise to a phenylacetaldehyde product (TP1), followed by a further oxidation  
325 process to convert the aldehyde group to a carboxyl group. Pathway II corresponded  
326 to the debromination process, leading to the generation of TP3. It was noteworthy that  
327 TP3 exhibited a relatively strong signal in the mass spectrum (Fig. S7), indicating that  
328 the yield of this product was relatively high during MF photolysis. Subsequently, TP3  
329 could further undergo methyl oxidation and aldehyde oxidation to produce TP4 and  
330 TP5 sequentially. Such process has been previously reported by López-Fernández et  
331 al. (2018) in the photolysis process of MF. Pathway III corresponded to the  
332 substitution of bromine by a hydroxyl group to give TP6, then, the methyl group on



333 TP6 could sequentially be oxidized to form TP7 and TP8.

334 Furthermore, it has been well documented that for the photochemical  
335 transformation of carbonyl chemicals, Norrish type I and II reactions were proposed  
336 to take place through which fission of the carbon-carbon bond would occur at the  $\alpha$ -  
337 and  $\gamma$ -positions, leading to the formation of bond cleavage or intramolecular  
338 cyclization products, respectively (Turro, 1978). However, in the present study, none  
339 of the above-mentioned products were identified by mass searching from the total ion  
340 chromatography (TIC) spectra; instead, the dominated photolysis pathway of MF was  
341 proposed as debromination process, which would be discussed in detail in the  
342 following section.

#### 343 **Fig. 4.**

#### 344 *3.5 Photo-induced debromination*

345 As mentioned, debrominated product (TP3) were found to be the major  
346 photoproduct of MF, indicating that C-Br bond dissociation was an important path of  
347 mechanistic explanation. This bond cleavage might take place either *via* a homolytic  
348 process to give a carbon-based benzoylbzyl radical and bromine atom, or through a  
349 heterolytic process to generate a corresponding benzyl cation and bromide anion.

350 In order to gain a detailed insight into the photolysis mechanism of MF, LFP  
351 experiments were conducted to identify the potential transient intermediates involved  
352 in the photochemical process. Fig. 5 exhibited the time-dependent transient absorption  
353 spectrum of 0.25 mM MF in ACN after 266 nm laser excitation. As can be seen, a  
354 broad transient absorption band with maximum absorption around 345 nm was

355 obtained at the pulse end, and the presence of two different triplet scavengers, namely,  
356 oxygen and acrylamide were found to hardly affect its formation, indicating that this  
357 species could not be assigned to the triplet excited state of MF (Fig. S10). In  
358 accordance, the triplet excited states of benzophenone (BP) and some of its  
359 derivatives were reported to show maximum absorption around 525 nm (Ryuzi et al.,  
360 1997) (Fig. 5(d)). We looked after a signal in this wavelength range, but absorbances  
361 were very weak (Fig. 5(c)). On the other hand, the spectrum analogy of our transient  
362 ( $\lambda_{\max} = 345$  nm) with those of *m*-benzoylbenzyl radical (*m*-BBR,  $\lambda_{\max} = 335$  nm) and  
363 *p*-benzoylbenzyl radical (*p*-BBR,  $\lambda_{\max} = 320$  nm) (Yamaji et al., 2007) prompted us to  
364 assign it to the benzoylbenzyl radical of MF (MBR). Yamaji et al. (2007) reported that  
365 upon 266 nm excitation in LFP experiments, *m*-bromomethylbenzophenone  
366 (*m*-BMBP) would be excited to generate *m*-BBR, and this process could be achieved  
367 via an extremely fast  $\omega$ -cleavage of both lowest singlet (S1) and triplet (T1) *m*-BMBP.  
368 In their case also, triplet *m*-BMBP could be hardly be detected by LFP (Yamaji et al.,  
369 2007). However, differently from *m*-BBR, MBR was found to be short-lived,  
370 undergoing a fast decay within 0.05  $\mu$ s to give a relatively long-lived secondary  
371 intermediate (Fig. 5(a)). The shorter life-time of MBR might be attributed to the  
372 presence of methyl and methoxy substituents allowing fast intramolecular reactions to  
373 take place.

374 To further support the formation of MBR, DFT calculation were conducted to  
375 obtain the theoretical UV-Vis absorption of two potential intermediates, namely, MBR  
376 and the benzyl cation. The validation of this method was firstly checked by

377 calculating the absorption of parent MF. As seen, theoretical calculation exhibited a  
378 maximum absorption peak at 290 nm (Fig. S1), which was in a good agreement with  
379 the experimentally measured absorption peak at 292 nm (Fig. 2). In the case of MBR,  
380 calculation showed a maximum absorption peak around 350 nm (Fig. S11), matching  
381 well with the spectrum observed by LFP experiments (Fig. 5(a)). For the benzyl  
382 cation, the maximum absorption was calculated to be around 460 nm. Therefore, we  
383 have confirmed the homolytic cleavage of the C-Br bond of MF.

384 In addition, for the homolytic cleavage process, we further calculated the bond  
385 dissociation energy (BDE) of C-Br bond on the basis of  $\Delta H$  derived from  
386 thermochemical parameters from the optimized MF, MBR and bromine atom at an  
387 ideal condition (298.15 K and 1 atm). A BDE value for C-Br bond cleavage of MF  
388 was estimated to be 67.9 kcal mol<sup>-1</sup>, which was lower than that of the lowest singlet  
389 state (S1, 89.1 kcal mol<sup>-1</sup>) and triplet state (T1, 71.2 kcal mol<sup>-1</sup>). Based on the  
390 experimental and theoretical results, an energy diagram for the deactivation and bond  
391 dissociation processes of excited MF is depicted in Scheme.1. Similar to *m*-BMBP,  
392 the excited singlet state of MF produced an excited triplet state through intersystem  
393 crossing. Alternatively, S1 and T1 state could also undergo C-Br bond cleavage to  
394 produce MBR and bromine atom (Scheme. 1(a)). Bond dissociation from S1 was  
395 thermodynamically more favorable than from T1, and was proposed as the dominant  
396 pathway for C-Br bond cleavage.

397 Based on the products identification, DFT calculation and LFP experiments, the  
398 detailed debromination mechanism can be tentatively discussed. Once MBR was

399 generated, the formation of TP3 required access to hydrogen atoms. They cannot be  
400 supplied by water, while the methyl group on the ortho-position was likely to act as a  
401 good hydrogen donor. In this case MBR might undergo an extremely fast  
402 intramolecular rearrangement process, leading to the rapid disappearance of MBR and  
403 to the formation of the corresponding secondary transient species (Fig. 5(b)). The new  
404 produced intermediate can experience an intermolecular hydrogen extraction from  
405 another MF molecule, giving TP3, or undergo a series of further oxidation processes  
406 to generate the methyl oxidation products.

407 In conclusion, a detailed diagram of MF photolysis process is illustrated in  
408 Scheme. 1(b). Specifically, upon irradiation, MF would be excited to singlet state,  
409 which could either directly break the C-Br bond or undergo ISC process to give  $^3\text{MF}^*$ .  
410 Similarly,  $^3\text{MF}^*$  undergoes C-Br bond homolytic cleavage reaction to give rise to  
411 MBR and  $\cdot\text{Br}$ . Meanwhile,  $^3\text{MF}^*$  can also transfer its energy to dissolved oxygen,  
412 resulting in the formation of  $^1\text{O}_2$ , which in turn leads to the further oxidation of MF.

413 **Fig. 5.**

414 **Scheme.1.**

### 415 *3.6 Toxicity prediction during MF transformation*

416 In the present study, the acute and chronic toxicity of MF and photoproducts to  
417 fish, daphnia and green algae was evaluated through the ECOSAR procedure (Wei et  
418 al., 2018). The toxicity was classified according to the Globally Harmonized System  
419 of Classification and Labelling of Chemicals (Liu et al., 2019).

420 The acute toxicity values of MF were determined to be 1.20 mg L<sup>-1</sup>, 0.88 mg L<sup>-1</sup>  
421 and 1.85 mg L<sup>-1</sup> for fish, daphnia and green algae, respectively. These results showed  
422 that MF was toxic for aquatic species, especially with lower trophic organisms such as  
423 daphnia (< 1.0 mg L<sup>-1</sup>). The chronic toxicity values (Chv) of MF were predicted to be  
424 0.16 mg L<sup>-1</sup>, 0.17 mg L<sup>-1</sup> and 0.85 mg L<sup>-1</sup> for fish, daphnia and green algae,  
425 respectively, suggesting that MF was more likely to have a chronic toxic effect on  
426 organisms. Simultaneously, the trend in chronic toxicity for the three different trophic  
427 levels was consistent with acute toxicity. In summary, MF was obviously toxic to  
428 aquatic species and can disrupt the ecological balance of the aquatic environment,  
429 thus the detection and control of MF in the environment should be given more  
430 attention.

431 Predicting the toxicities of intermediate products during MF transformation was  
432 also particularly important (Karci. and Akin., 2014). Therefore, we calculated the  
433 toxicity changes of the intermediate products in the three MF photolysis pathways for  
434 fish, Daphnia and green algae, and the results were shown in Fig. 6. In ECOSAR  
435 predictions, toxicity actually decreases if the toxicity parameter (e.g., Lethal  
436 Concentration 50 (LC50)) decreases by at least one order of magnitude. From this  
437 perspective, the acute toxicity of intermediate products showed a decreasing trend  
438 only for Daphnia. For fish, all the debromination products (TP3 and TP6) and the  
439 methyl aldolization products (TP1, TP4 and TP7) were in the same order of  
440 magnitude of acute toxicity as MF. However, the acute toxicity of the methyl  
441 carboxylation products (TP2, TP5 and TP8) was directly decreased by two orders of

442 magnitude. The acute toxicity variation for green algae was similar with fish, but the  
443 toxicity of both TP6 and TP7 in the OH-debromination pathway was one order of  
444 magnitude higher than MF, indicating that toxicity was enhanced. A little different  
445 from the acute toxicity, the chronic toxicity of both debromination pathways showed a  
446 continuous decreasing trend only for green algae (except TP1). For fish and daphnia,  
447 the chronic toxicity of TP1, TP3, TP4, TP6 and TP7 remained in the same order of  
448 magnitude as MF. Aldehyde groups are known to be toxic to organisms through  
449 chemical bonding with amino bearing biomolecules such as enzymes, proteins,  
450 condensates, nucleic acid derivatives etc. *via* Schiff bases (Slomkowski, 1998;  
451 Sokolsky et al., 2006). This might be responsible to higher toxicity of intermediate  
452 products containing aldehyde groups. Notably, further oxidation of the aldehyde  
453 products to the carboxylate products decreased the toxicity rapidly. All the above  
454 results indicated that the toxicity of some intermediate products of three photolysis  
455 pathways may maintain or even increase, but the toxicity of the final  
456 carboxyl-containing product is greatly reduced, photodegradation is still a method that  
457 can safely reduce the ecotoxicity of MF in aquatic environment.

### 458 **Fig. 6.**

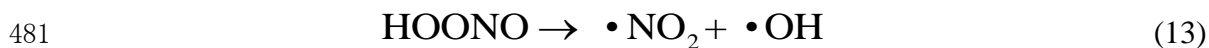
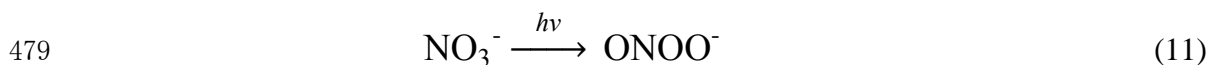
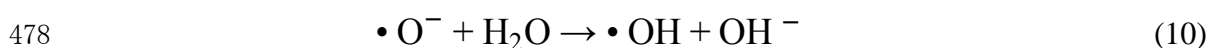
#### 459 *3.7 Effects of natural water constituents*

##### 460 *3.7.1 Effect of nitrate*

461 Nitrate is one of the most abundant anions in the aquatic environment whose  
462 photochemical reactivity can affect the photochemical fate of the organic  
463 contaminants (Mack and Bolton, 1999; Zuo et al., 2006). In the present study, the

464 photodegradation experiments of MF were conducted in 25 mL aqueous solutions  
 465 containing 20  $\mu\text{M}$  substrates with different nitrate concentrations (0, 5, 20 and 50 mM)  
 466 under irradiation for 8 h and the results are presented in Fig. 7(a).

467 The photolysis rate of MF was observed to be significantly accelerated as the  
 468 nitrate concentration increased. The rate constants were 0.055, 0.080, 0.143 and 0.167  
 469  $\text{h}^{-1}$  for nitrate concentrations of 0, 5, 20 and 50 mM, respectively.  $\bullet\text{OH}$  generated by  
 470 nitrate photolysis is one of the major ROS accounting for the attenuation of pollutants  
 471 in natural waters (George et al., 1988; Monica et al., 2013). Eqs (9)-(13) show how  
 472 solar irradiation of nitrate leads to the formation of  $\bullet\text{NO}_2$  and  $\bullet\text{OH}$  directly and  
 473 indirectly *via* its photoisomerization to peroxyxynitrite/peroxyxynitrous acid (Kotnik et al.,  
 474 2016; Vione et al., 2009). In this work, the  $\bullet\text{OH}$  generated by nitrate photolysis was  
 475 identified by EPR analysis (Fig. S12(a)), thus was proposed to be responsible for the  
 476 decay of MF.



### 482 3.7.2 Effect of bicarbonate

483 Bicarbonate is the major anion responsible for water alkalinity. Bicarbonate has  
 484 been reported to play an important influence on the indirect photolysis of organic  
 485 pollutants in natural waters (Huang and Scott, 2000). Experimental results show that

486 the presence of bicarbonate barely affected the photolysis process of 20  $\mu\text{M}$  MF (Fig.  
487 7(b)). The corresponding rate constants were found to be equal to 0.059, 0.064, 0.059  
488 and 0.062  $\text{h}^{-1}$  as the bicarbonate concentration increased from 0 to 20 mM.  
489 Bicarbonate can interact with  $\bullet\text{OH}$  to form carbonate radicals ( $\text{CO}_3\bullet^-$ ) (Eq. (14))  
490 (Huang and Scott, 2000), which is a strong electrophile that can rapidly oxidize  
491 phenolic compounds (Neta et al., 1988). However, our quenching experiments ruled  
492 out the involvement of  $\bullet\text{OH}$  in the direct photolysis of MF.



494 In addition, the presence of bicarbonate can also affect the photochemical  
495 transformation of organic compounds *via* altering the solution pH (Ji et al., 2012).  
496 However, this effect is expected to be not important due to the pH-independent  
497 photolysis of MF (*vide supra*).

### 498 *3.7.3 Effect of humic acid*

499 Humic substances are ubiquitous in soils and surface waters which are formed by  
500 decomposition of living organisms. In the aquatic environment, they are able to  
501 compete with pollutants to absorb photons for photolysis as an inner filter (light  
502 screener) (Luciano et al., 2009; Monica et al., 2003). Meanwhile, as a photosensitizer,  
503 they are capable of affecting the persistence of organic pollutants in the environment  
504 through energy transfer or reaction with photochemically produced reactive  
505 intermediates (PPRI) (Manjun et al., 2006; Richard et al., 1997; Yong et al., 2009;  
506 Zepp et al., 1985). In view of this, the photolysis of 20  $\mu\text{M}$  MF was conducted in the  
507 presence of humic acids (HA) at a concentration ranging from 0 and 20  $\text{mg L}^{-1}$ , and



508 the results are shown in Fig. 7(c).

509 The kinetic rate constants were determined to be 0.056, 0.064, 0.094, and 0.139  
510  $\text{h}^{-1}$  at HA concentrations 0, 2, 5 and 20  $\text{mg L}^{-1}$ , respectively. Compared with ultrapure  
511 water controls, the photodegradation rate of MF in the presence of HA was  
512 significantly higher. HA was a macromolecule with a complex structure, containing a  
513 large number of chromophores comprised of benzene ring, carboxyl, carbonyl, and  
514 methoxyl moieties (Laurentiis et al., 2013). The HA-enhanced photolysis of MF may  
515 occur either through energy transfer from the excited HA to the ground state MF, or  
516 *via* oxidation by PPRI, such as  $\bullet\text{OH}$  and  $^1\text{O}_2$ , which promote the photolysis of MF  
517 (Rajib et al., 2011). The involvement of  $\bullet\text{OH}$  and  $^1\text{O}_2$  in the photolysis of MF in the  
518 presence of HA was confirmed by our EPR analyses, as illustrated in Fig. S12(b).

519 From this section, it is clear that natural water constituents such as nitrate and  
520 humic acid have significant impacts on the photodegradation rate of MF. Therefore,  
521 direct photolysis is not expected to be the main photodegradation pathway of MF in  
522 the environment, and further studies are required to better understand its  
523 photoreactivity.

524 **Fig. 7.**

#### 525 **4. Conclusions**

526 In this study, the photodegradation of MF in aqueous solution under simulated  
527 solar irradiation was investigated, including photolysis kinetics, reactive intermediates,  
528 products identification, photolysis pathways and mechanisms. Under simulated sunlit,  
529 direct photolysis rate constant of MF in aqueous solution was  $0.056 \pm 0.003 \text{ h}^{-1}$ ,

530 corresponding to a half-life of  $12.4 \pm 0.6$  h, indicating that photochemical degradation  
531 was an important pathway for the removal of the fungicide MF in nature. Three  
532 different pathways were proposed based on HR-MS analysis, including methyl  
533 oxidation, debromination and replacement of Br by OH group. Among them  
534 debromination process was identified as the main path. Homolytic cleavage of the  
535 C-Br bond from both  $^1\text{MF}^*$  and  $^3\text{MF}^*$  is likely to take place. MF is also likely  
536 oxidized by  $^1\text{O}_2$  produced by energy transfer from  $^3\text{MF}^*$  to  $\text{O}_2$ .  $\text{NO}_3^-$  and humic acid  
537 were found to enhance the decay of MF, while  $\text{HCO}_3^-$  exhibited no significant effect  
538 on MF photolysis. Toxicity assessment revealed that photochemical transformation  
539 was an efficient process to reduce the ecotoxicity of MF. This study provided  
540 important information for the understanding of photolytic behavior of MF in the  
541 aqueous environment.

#### 542 **Declaration of competing interest**

543 There is no declaration of interest in this investigation. The authors declare no  
544 competing financial interest.

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