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New insights into the mechanism of phosphate release during particulate organic matter photodegradation based on optical and molecular signatures

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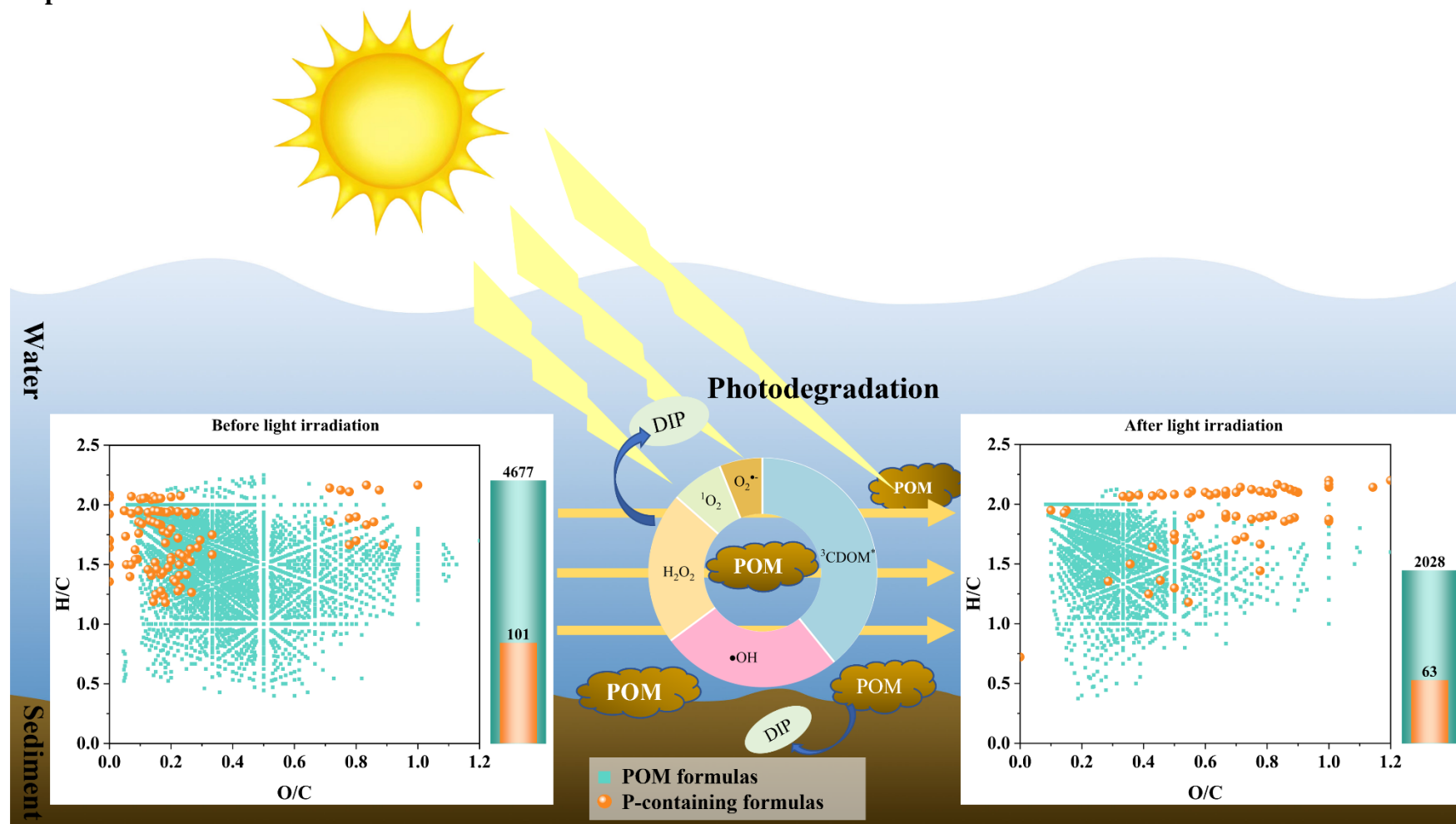
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Graphical abstract



Highlights:

- Phosphate release during POM photodegradation was characterized by FT-ICR MS.
- Organic phosphorus in POM participated in the photochemical reactions.
- Unsaturated P-containing formulas in POM were preferentially photodegraded.
- ³CDOM* was mainly responsible for POM photodegradation in aquatic environment.

1 New insights into the mechanism of phosphate release during
2 particulate organic matter photodegradation based on optical
3 and molecular signatures

4 Minli Guo^a, Xiaolu Li^a, Yi Wang^a, Yunlin Zhang^b, Qinglong Fu^c,

5 Arnaud Huguet^d, Guanglong Liu^{a*}

6 **Affiliations**

7 ^aKey Laboratory of Arable Land Conservation (Middle and Lower Reaches of Yangtze
8 River), Ministry of Agriculture and Rural Affairs, College of Resources and
9 Environment, Huazhong Agricultural University, Wuhan 430070, China

10 ^bState Key Laboratory of Lake Science and Environment, Nanjing Institute of
11 Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

12 ^cSchool of Environmental Studies, China University of Geosciences, Wuhan 430074,
13 China

14 ^dSorbonne Université, CNRS, EPHE, PSL, UMR METIS, F-75005 Paris, France

15

16 *Corresponding author.

17 *E-mail address:* liugl@mail.hzau.edu.cn (Guanglong Liu)

18

19

20 **Abstract**

21 Phosphate release from particulate organic matter (POM) dominates phosphorus
22 (P) cycling in aquatic ecosystems. However, the mechanisms underlying P release from
23 POM remain poorly understood because of complex fractionation and analytical
24 challenges. In this study, the release of dissolved inorganic phosphate (DIP) during
25 POM photodegradation was assessed using excitation–emission matrix (EEM)
26 fluorescence spectroscopy and Fourier transform ion cyclotron resonance mass
27 spectrometry (FT-ICR MS). POM in suspension was significantly photodegraded under
28 light irradiation, concomitantly with the production and release of DIP in the aqueous
29 solution. Chemical sequential extraction revealed that organic phosphorus (OP) in POM
30 participated in photochemical reactions. Moreover, FT-ICR MS analysis revealed that
31 the average molecular weight of P-containing formulas decreased from 374.2 to 340.1
32 Da. Formulas containing P with a lower oxidation degree and unsaturation were
33 preferentially photodegraded, generating oxygen-enriched and saturated formula
34 compounds, such as protein- and carbohydrate-like P-containing formulas, benefiting
35 further utilization of P by organisms. Reactive oxygen species played an important role
36 in the photodegradation of POM, and excited triplet state chromophoric dissolved
37 organic matter ($^3\text{CDOM}^*$) was mainly responsible for POM photodegradation. These
38 results provide new insights into the P biogeochemical cycle and POM
39 photodegradation in aquatic ecosystems.

40 **Keywords:** Particulate organic matter; Photodegradation; Phosphate; FT-ICR MS;

41 Reactive oxygen species

42 **Abbreviations**

43 POM, particulate organic matter; DIP, dissolved inorganic phosphate; EEM, excitation–
44 emission matrix; FT-ICR MS, Fourier transform ion cyclotron resonance mass
45 spectrometry; OP, organic phosphorus; ³CDOM*, excited triplet state chromophoric
46 dissolved organic matter; ROS, reactive oxygen species; OM, organic matter; DOP,
47 dissolved organic phosphorus; SPE, solid phase extraction; TOC, total organic carbon;
48 TMP, 2,4,6-trimethyphenol; FFA, furfuryl alcohol; •OH, hydroxyl radical; O₂^{•-}
49 superoxide anion; ¹O₂, singlet oxygen; KMD, Kendrick mass defect; DBE, double bond
50 equivalent; CNs, carbon numbers; DOM, dissolved organic matter
51

52 **1. Introduction**

53 Frequent water blooms caused by eutrophication pose a major threat to ecological
54 health and drinking water safety (Hou et al., 2022; Zhang et al., 2022b). Phosphorus (P)
55 is the key element involved in eutrophication and algal blooms (Conley et al., 2009;
56 Schindler et al., 2016). After the efficient control of exogenous P input, the rapid
57 transformation of endogenous P has become an important source of P compensation
58 (Xu et al., 2018). The transport and transformation of particulate organic matter (POM),
59 a carrier of endogenous P, can greatly impact the amount of bioavailable P in water
60 (Joshi et al., 2015; Li et al., 2017a). Accelerated eutrophication of water bodies
61 accumulates a large amount of POM, and the decomposition of POM through
62 mineralization or abiotic processes can release a large amount of dissolved nutrients,
63 compensating for the P demand during phytoplankton growth.

64 Traditionally, research has been focused on the biomineralization process of POM,
65 in which microorganisms play an important role (Zhang et al., 2022a). Recent studies
66 have revealed that photochemical transformation is also important for the fate of POM
67 (Harfmann et al., 2021; Helms et al., 2014; Lee et al., 2021; Liu and Shank, 2015). The
68 photochemical transformation of POM caused by solar radiation can change its
69 chemical composition and molecular size and ultimately affect the biogeochemical
70 processes of carbon (C), nitrogen (N), and P (Hu et al., 2022; Lee et al., 2023; Mayer
71 et al., 2006). Previous studies have also confirmed that POM can be photodegraded and
72 release dissolved nutrients and that this process can be affected by irradiation conditions,
73 POM properties, reactive oxygen species (ROS), and other factors (Hu et al., 2021;

74 Shank, 2011). Our previous research revealed that suspended particles in shallow lakes
75 can release dissolved inorganic phosphate (DIP) under sunlight exposure (Guo et al.,
76 2020; Li et al., 2019). Its release mechanism involves photolysis, enzymatic hydrolysis
77 of organic phosphorus (OP), and catalytic hydrolysis by minerals (Baldwin et al., 1995;
78 Klein et al., 2019; Wan et al., 2019). However, the extractants used in chemical
79 sequential extraction lack specificity (Zhu et al., 2013). Moreover, the peak spectrum
80 in ^{31}P -nuclear magnetic resonance (^{31}P -NMR) is easy to overlap (Worsfold et al., 2008),
81 resulting in insufficient understanding of the mechanism of DIP release during POM
82 photodegradation.

83 Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) is a
84 robust tool for analyzing complex organic matter (OM) at the molecular level, despite
85 its complexity and heterogeneity. This ultra-high-resolution technique is powerful to
86 determine the molecular composition of complex environmental samples (Bahureksa
87 et al., 2021) and has been widely used for the molecular characterization of OM in
88 various types of environmental samples (Kellerman et al., 2015; McDonough et al.,
89 2022; Singer et al., 2012; Wagner et al., 2015). Because OP molecules in the
90 environment are composed of ester (C-O-P) and carbon phosphorus (C-P) (Ni et al.,
91 2022), a few scholars have successfully used FT-ICR MS to analyze the source,
92 composition, and transformation of OP in the environment (Brooker et al., 2018; Gao
93 et al., 2021; Ni et al., 2021). The use of this technology greatly helps understand the P
94 biogeochemical cycle at the molecular level.

95 This study aimed to investigate DIP release resulting from POM photodegradation

96 in water, focusing on molecular changes occurring during this process. POM
97 photodegradation and DIP release were assessed through a simulated light experiment.
98 The molecular weight distribution, species, and structure of P-containing formulas in
99 POM during photodegradation were analyzed using FT-ICR MS. In addition, ROS
100 involved in POM photodegradation were investigated using a reactive oxygen
101 molecular probe to obtain key results on the molecular mechanisms underlying DIP
102 release during the photochemical transformation of POM.

103 **2. Materials and Methods**

104 **2.1. Photodegradation experiments**

105 A suspension of lake water and sediments was used to simulate the
106 photodegradation of POM in shallow lakes. Lake water and sediment samples were
107 collected from Lake Nanhu (Wuhan, China) on March 17, 2019. Basic information on
108 Lake Nanhu is provided in the Supporting Information. The weather was bright, and
109 the wind speed was 3.4–5.6 m/s in the week before sampling. The water sample was
110 obtained from the overlying 10 cm surface of the lake. The top 10 cm sediment was
111 collected using a Peterson grab collector. All water and sediment samples were screened
112 for impurities and were mixed, covered with ice packs, and stored at 4 °C and –20 °C,
113 respectively. The overlying water samples collected from each sampling site were
114 filtered using 0.45 µm filters (Jinteng Experimental Equipment Co., Ltd, Tianjin, China)
115 and stored at 4 °C. The basic physical and chemical parameters of the lake water and
116 sediment samples are summarized in Table S1.

117 Wet sediment (4 g, moisture content: 34.63% ± 0.05%) was added to filtered lake

118 water (1 L) in a beaker and completely resuspended by stirring at 350 rpm for 16 h. The
119 suspension (approximately 500 mg/L suspended particles) was then allowed to settle
120 for 20 min, and the top 20 cm was collected for conducting photodegradation
121 experiments in a rotating photoreactor (Phchem III, Newport Corporation, Beijing,
122 China). A schematic of the experimental setups has been provided in our previous study
123 (Guo et al., 2020). A high-pressure mercury lamp (300 W) was used to provide light,
124 and a UV light photometer (UV254, Newport Corporation, Beijing, China) was used to
125 measure the irradiance on the surface of the quartz tubes. The irradiation intensity was
126 measured to be approximately 3.5 mW/cm², which was close to that on the lake water
127 surface on a midsummer day. The internal temperature of the reactor was maintained at
128 35 ± 2 °C by connecting it with a quartz cold trap and a ventilation device. Before light
129 irradiation, the magnetic stirrer was turned on overnight to ensure that the particles in
130 suspension in the photochemical reaction tubes were in a completely suspended state
131 and weakly adsorbed P was completely released. Samples were collected at scheduled
132 time intervals to analyze the concentration of DIP. Dark treatment was set as a control
133 and performed under the same conditions but by wrapping in tinfoil. To clarify the
134 contribution of POM photodegradation to DIP concentrations in water, filtered lake
135 water samples under light and dark treatments were used as controls.

136 **2.2. Determination of P content**

137 The amount of DIP released from POM photodegradation was determined using
138 the molybdenum blue colorimetric method (Murphy and Riley, 1962). The dissolved
139 total phosphorus (DTP) content was measured after digestion with 5% potassium

140 persulfate. The dissolved organic phosphorus (DOP) content was calculated by
141 subtracting DIP from DTP.

142 To assess the changes in P components during POM photodegradation, the P
143 fractions before and after light irradiation were analyzed by chemical sequential
144 extraction, as proposed by Rydin (2000). Details of the method can be found in Fig. S1.
145 Using this method, P was separated into six groups: $\text{NH}_4\text{Cl-P}$ (loosely adsorbed P), BD-
146 P (P forms sensitive to low redox potential, adsorbed to iron and manganese), NaOH-
147 rP (P exchangeable with OH^- , mainly aluminium oxide), NaOH-nrP (OP), HCl-P (P
148 forms sensitive to low pH, such as apatite), and Res-P (refractory organic P and the inert
149 inorganic P fraction).

150 **2.3. Pretreatment of POM and excitation–emission matrix (EEM) analysis**

151 To evaluate the photodegradation of POM in suspension under light irradiation,
152 the fluorescence spectrum of POM was determined. POM was extracted as described
153 previously (He et al., 2016). In brief, the suspended particles were collected using 0.45
154 μm filters (Jinteng Experimental Equipment Co., Ltd, Tianjin, China) before and after
155 light irradiation for 58 h and then freeze dried before grinding. Next, 1.0 g of freeze-
156 dried suspended particles were soaked in 0.1 mol/L of NaOH solution and shaken at
157 180 rpm at 25 °C for 24 h. The solutions were then centrifuged at 10,000 rpm for 20
158 min, and the supernatants were filtered through precombusted 0.22 μm glass fiber filters
159 (Jinteng Experimental Equipment Co., Ltd, Tianjin, China). The filtrates were collected
160 and stored at 4 °C for no more than 2 weeks until other analyses and solid phase
161 extraction (SPE). The concentration of total organic carbon (TOC) was measured by a

162 TOC analyzer (Vario TOC Cube, Elementar, Germany).

163 The fluorescence spectroscopy of POM was obtained by scanning at an excitation
164 wavelength of 220–450 nm (2 nm interval) and emission wavelength of 250–600 nm
165 (1 nm interval) using the Shimadzu fluorescence spectrophotometer RF5301.
166 Fluorescence regional integration (FRI) and parallel factor (PARAFAC) modeling
167 analyses of the POM extract were performed on MATLAB R2018b. EEM fluorescence
168 spectroscopy data were calibrated using an ultrapure water blank.

169 **2.4. SPE and FT-ICR MS analysis**

170 SPE was performed using a previously described method (Brooker et al., 2018).
171 In brief, 500 mg Bond Elut PAX cartridges (Agilent Technologies, 12257506) were
172 used to extract POM formulas and P-containing formulas from all samples. The
173 cartridges were first washed with 20 mL LC–MS-grade methanol (Fisher, USA) and
174 then washed with 20 mL of ultrapure water. While still wet, the filtrates, which were
175 adjusted to pH ~10 using NH₄OH and HCOOH, were gravity filtered through
176 conditioned PAX cartridges to collect and concentrate OM with molecular weight <
177 1000 Da. The cartridges were rinsed with 20 mL of 1% NH₄OH for the complete
178 removal of Cl⁻ and other ions to minimize the interference of Cl on the formula
179 assignment of P-containing formulas. Next, the cartridges were dried with ultrapure N₂
180 gas. The samples were eluted from the cartridges using 10 mL of LC–MS-grade
181 methanol, followed by 10 mL of methanol with 5% formic acid. The elutes were
182 combined into amber glassware and dried with N₂ gas. After redissolving the elutes
183 using LC–MS-grade methanol, a 9.4 T Bruker Apex Ultra FT-ICR MS instrument

184 equipped with an Apollo II electrospray ion source was used for FT-ICR MS analysis
185 in the negative-ion mode. Detailed information on the operating parameters and data
186 processing is provided in the Supporting Information. In brief, a 1 mL aliquot of
187 leachates was dried with N₂ gas and diluted using 50 mL of ultrapure water to measure
188 the extraction efficiency of PAX cartridges.

189 Van Krevelen diagrams are typically used for FT-ICR MS data comparison. They
190 can distinguish biomolecular chemical classes using O/C and H/C plots (Kim et al.,
191 2003; Ohno et al., 2010). According to van Krevelen diagrams, compounds are
192 generally classified into seven categories (Feng et al., 2016; Ni et al., 2021): (1) lipids
193 ($1.5 \leq H/C \leq 2$, $0 \leq O/C \leq 0.3$), (2) proteins ($1.5 \leq H/C \leq 2.2$, $0.3 \leq O/C \leq 0.67$), (3)
194 carbohydrates ($1.5 \leq H/C \leq 2.4$, $0.67 \leq O/C \leq 1.2$), (4) unsaturated hydrocarbons (0.7
195 $\leq H/C \leq 1.5$, $0 \leq O/C \leq 0.1$), (5) lignins ($0.7 \leq H/C \leq 1.5$, $0.1 \leq O/C \leq 0.67$), (6) tannins
196 ($0.5 \leq H/C \leq 1.5$, $0.67 \leq O/C \leq 1.2$), and (7) condensed aromatic structures ($0.2 \leq H/C$
197 ≤ 0.7 , $0 \leq O/C \leq 0.67$).

198 **2.5. Capture and detection of ROS**

199 To determine the contribution of different ROS types on POM photodegradation, a
200 series of sacrificial experiments were performed. Isopropanol (IPA, 0.2%), superoxide
201 dismutase (SOD, 1200 U/L), catalase (CAT, 20 U/L), 2,4,6-trimethylphenol (TMP, 10
202 mM), and furfuryl alcohol (FFA, 5 mM) were added to quench any hydroxyl radical
203 ($\bullet\text{OH}$), superoxide anion ($\text{O}_2^{\bullet-}$), H₂O₂, excited triplet state chromophoric dissolved
204 organic matter ($^3\text{CDOM}^*$), and singlet oxygen ($^1\text{O}_2$) (Zeng et al., 2022; Zhang et al.,
205 2019; Zheng et al., 2022), respectively. $\text{O}_2^{\bullet-}$ was qualitatively analyzed by determining

206 the content of diformazan (produced by $O_2^{\bullet-}$ and nitro blue tetrazolium chloride) at 530
207 nm using a UV spectrophotometer (Zong et al., 2020). The generated H_2O_2 was
208 quantified by the colorimetric method using cerous sulfate. The selective probe
209 compound FFA, at an initial concentration of 1 mM (Song and Jiang, 2020), was used
210 to capture 1O_2 . The probe molecule for $^3CDOM^*$ -TMP was added to the reaction
211 solution at an initial concentration of 1 mM (Song and Jiang, 2020). To measure the
212 $\bullet OH$ concentration, benzoic acid (BA) (1 g/L) was added to the system (Chen et al.,
213 2017). The concentrations of FFA, TMP, and *para*-hydroxybenzoic acid (PBA)
214 (generated by $\bullet OH$ and BA) were determined by high-performance liquid
215 chromatography (HPLC, Agilent 1260). The detailed parameters of HPLC analyses are
216 listed in the Supporting Information.

217 **3. Results and Discussion**

218 **3.1. Photodegradation of POM and variation in P content**

219 The fluorescence spectroscopy of POM under light irradiation and dark treatment
220 is shown in Fig. S2. The signal intensity and region volume sharply decreased after
221 light irradiation, while almost no change was noted after dark treatment (Fig. S2 and
222 Table S2), indicating that the fluorophoric POM components were degraded under light
223 irradiation. The concentration of TOC in the POM extract decreased from 198.78 mg/L
224 to 93.68 mg/L after light irradiation, and the degradation rate reached to 52.87%. In
225 addition, the PARAFAC model with two to seven components was assessed. Based on
226 the residual analysis and split-half analysis, three components, including the protein-
227 like component C1, microbial humic-like component C2, and terrestrial humic-like

228 component C3, were determined as the best fit (Fig. 1). The maximum fluorescence
229 intensity (F_{\max}) values of these three components significantly decreased after light
230 irradiation. The microbial humic-like component C2 showed the highest decrease
231 (55.3%), followed by the terrestrial humic-like component C3 (50.5%) and protein-like
232 component C1 (42.6%), indicating the photodegradation property of POM. This
233 property can affect the composition and fate of POM, thereby affecting the
234 concentration of bioavailable nutrients in aquatic environments and the eutrophication
235 process.

236 Fig. 2 shows the release of DIP during the photodegradation of POM in suspension.
237 The concentration of DIP in the suspension increased under both light and dark
238 treatments. In the dark treatment group, DIP increased by 0.06 mg/L, mainly because
239 of the microbial mineralization of POM. In contrast, DIP increased by 0.35 mg/L in the
240 light treatment group; this was approximately sixfold higher than that in the dark
241 treatment group, indicating that more POM was degraded during light treatment.
242 Considering the amount of DIP released in the filtered lake water after light treatment
243 (only 0.03 mg/L) (Fig. 2a), it could be confirmed that POM was a significant potential
244 source of P in water. Kinetic analysis revealed that DIP release during POM
245 photodegradation fit the pseudo-second order reaction (Table S3 and Fig. S3),
246 indicating that intermediates were produced. The analysis of DOP concentration during
247 the reaction process also revealed that as the irradiation time increased, the DOP
248 concentration initially increased and then gradually decreased (Fig. S4), indicating that
249 DOP may play a more intermediate role during the photodegradation of POM. To

250 further clarify the effect of microorganisms on phosphate release during POM
251 degradation, flow cytometry was performed to determine the number of
252 microorganisms (living and dead bacteria) in the resuspended samples (Fig. S5 and
253 Table S4). The number of microorganisms during light treatment was lower than that
254 during dark treatment after 10 h, indicating that the increase in DIP concentration during
255 light treatment was due to the photochemical degradation of POM.

256 To determine the P components involved in the photodegradation of POM,
257 chemical sequential extraction was performed to analyze the P components in POM.
258 The contents of BD-P and NaOH-rP, important components of the P pool in POM, did
259 not change significantly before and after light irradiation, while that of NaOH-rP only
260 increased slightly (Fig. 2b). These findings suggest that BD-P and NaOH-rP are not the
261 sources of DIP release in solution. The NaOH-rP component (organic bound P) of
262 POM significantly decreased after light irradiation (Fig. 2b), again indicating that OP
263 in POM degraded during light irradiation. Surprisingly, the Res-P content also
264 decreased significantly after light irradiation. Res-P consists of refractory OP and inert
265 inorganic P (Rydin, 2000). Although inert OP in Res-P is difficult to be biodegraded
266 (Benitez-Nelson, 2000), it can still undergo photochemical decomposition.

267 **3.2. Variations in molecular characteristics of OP**

268 The molecular weight distributions of POM and P-containing formulas in POM
269 before and after light irradiation are presented in Fig. 3. The median molecular mass of
270 POM and P-containing formulas decreased from 365, 381 Da to 339, 335 Da, indicating
271 that light irradiation resulted in the conversion of POM and P-containing formulas into

272 small molecules. The average molecular weight of P-containing formulas was 374.2 Da
273 (Table S5), which is close to that reported by Ni et al. (2021). However, the number of
274 P-containing formulas detected in our sample (101) was lower than that reported by Ni
275 et al (75–670) (Ni et al., 2021). This may be related to the sample composition,
276 pretreatment process, and data analysis.

277 The changes in P-containing formulas in POM before and after light irradiation are
278 shown in Fig. 4. Before light irradiation, most P-containing formulas were lipid-, lignin-,
279 and carbohydrate-like P-containing formula compounds, with a relative abundance (RA)
280 of 46.5%, 18.8%, and 13.9%, respectively. This was followed by unsaturated
281 hydrocarbon-like (5.0%) and protein-like (2.0%) P-containing formula compounds. No
282 P-containing formulas were detected in the tannin- and condensed aromatic structure-
283 like formula compounds. After light irradiation, lipid-, unsaturated hydrocarbon-, and
284 lignin-like P-containing formula compounds were almost removed; their RA decreased
285 by 94.6%, 94.4%, and 48.3%, respectively (Fig. S6). Some protein- and carbohydrate-
286 like P-containing formula compounds with high O/C were newly generated (Fig. 4b).
287 The H/C_{wa} of P-containing formulas increased from 1.78 to 2.01 and their O/C_{wa}
288 increased from 0.20 to 0.75 after light irradiation (Table S5), indicating that P-
289 containing formulas exhibited higher saturation and stronger oxidation after light
290 irradiation. In summary, our results indicate that photochemical degradation tended to
291 remove P-containing formula compounds in POM with a low oxygen content, such as
292 lipid- and lignin-like P-containing formula compounds, and produce P-containing
293 formula compounds with a high oxygen content, such as protein- and carbohydrate-like

294 P-containing formula compounds.

295 To illustrate the compositional changes occurring within each subcategory of
296 molecules, photodegradable (peak lost), photogenerated (new peak), and photoresistant
297 (peak retained) P-containing formulas after light irradiation are plotted in Fig. 5.
298 Photodegradable P-containing formulas were mainly concentrated in the low O/C
299 region ($O/C < 0.3$) and high H/C region ($H/C > 1.0$). In contrast, photogenerated P-
300 containing formulas were mainly concentrated in the regions of $O/C > 0.3$ and $H/C >$
301 1.0 . The quantitative distributions of photodegradable, photogenerated, and
302 photoresistant P-containing formulas are presented in Fig. S7. These results suggest that
303 (i) less oxidized (i.e., lower O/C) and more aliphatic (i.e., higher H/C) compounds were
304 preferentially degraded to generate oxygen-rich molecules, explaining the significant
305 increase in O/C values, and (ii) the degradation of different O/C and H/C fractions in P
306 varied greatly. Therefore, the degradation potential of P-containing formula compounds
307 can be predicted by determining the O/C and H/C ratios of different P sources.

308 The transformation of P molecules can be inferred from the two-dimensional
309 display of Kendrick mass defect (KMD) versus nominal mass in FT-ICR MS (Hughey
310 et al., 2001). Molecules with the same KMD value correspond to compounds belonging
311 to the same class and type but with different numbers of functional groups (CH_2 groups
312 in this study, alkyl chain length). The difference between compounds with the same
313 KMD value but different mass values can be explained by the change in the number of
314 CH_2 , which represents the difference in the aliphatic properties of OM (Riedel et al.,
315 2012). In other words, the longer the alkyl chain length (i.e., the more the number of

316 CH₂ groups), the stronger is the aliphatic property of OM. An increase or decrease in
317 the number of alkyl chain substituents of their homologous formula will
318 correspondingly increase or decrease the molecular weight.

319 Before light irradiation, P-containing formulas were evenly distributed in the
320 range of 250–480 Da (Fig. 6). After light irradiation, P-containing formulas with
321 different alkyl chain lengths were removed to varying degrees. In the homologous series,
322 P-containing formulas with higher mass values (greater than 400 Da) were
323 preferentially removed, which corresponded to the decrease in their molecular weights
324 (Table S5). When the KMD values were <0.25, P-containing formulas were almost
325 removed, indicating lower removal selectivity by light irradiation. This implies that P-
326 containing formulas with high molecular weights (stronger aliphatic property) and low
327 KMD values are preferentially removed by light irradiation. In addition, the intensity
328 of P-containing formulas decreased to varying degrees after light irradiation, also
329 indicating the photodegradation of P-containing formulas.

330 Double bond equivalent (DBE) is an important parameter to clarify the
331 unsaturation and aromaticity of organic compounds (Gao et al., 2021). The distribution
332 of DBE and carbon numbers (CNs) can be used to analyze and compare the
333 characteristics of oxygen-containing molecules in OM (Bae et al., 2011). The
334 relationship between the DBE and CNs of P-containing formulas is plotted in Fig. S8.
335 Before light irradiation, P-containing formulas had a wide DBE range of 0–9; this range
336 is lower than that of P-containing formula compounds (0–14) reported by Gao et al. in
337 various treatment units of a wastewater treatment plant (Gao et al., 2021). This indicates

338 that the P-containing formulas in our study had low unsaturation and low aromaticity,
339 which also corresponded to the lower AI_{wa} . After light irradiation, formulas with $DBE >$
340 5 were largely removed and the DBE value sharply decreased, indicating an increase in
341 double bonds (unsaturated hydrocarbons) or the opening of the benzene ring
342 (lignin/carboxyl-rich acyclic molecules) (Liu et al., 2014), because formulas with $DBE >$
343 4 may contain one or more benzene rings. Moreover, DBE_{wa} decreased from 2.35 to
344 0.63 after light irradiation, indicating that the generated P-containing formulas became
345 more saturated and nonaromatic (e.g., protein- and carbohydrate-like P-containing
346 formula compounds); this also explains the sharp decrease in AI_{wa} and DBE_{wa} (Table
347 S5). This result also corresponded to that of the P-containing formulas presented in Fig.
348 5. P-containing formulas had a CN range of 6–27 before light irradiation. After light
349 irradiation, formulas with $CNs > 15$ were largely removed and the average CNs
350 decreased, suggesting a decrease in the average molecular weight of P-containing
351 formulas (Table S5) and indicating the breakage of C-O-P and/or C-P bonds by light
352 irradiation.

353 The P-containing formulas removed after light irradiation were characterized by a
354 low oxygen content (Fig. 5), while the generated P-containing formulas were rich in
355 oxygen and highly saturated. The removed P-containing formulas mainly included
356 lipid-like P-containing formula compounds with a low oxygen content and some
357 saturation, unsaturated hydrocarbon-like P-containing formula compounds with low
358 unsaturation, and lignin-like P-containing formula compounds with a low oxygen
359 content (Fig. 4). As lipids are usually related to algae-derived OM with high

360 bioavailability (Liu et al., 2020), they can be easily removed after light irradiation.
361 Previous studies considered lignin-like OM to be resistant (Hertkorn et al., 2006;
362 Mesfioui et al., 2012; Opsahl and Benner, 1997; Yuan et al., 2017). However, we found
363 that part of the lignin-like P-containing formula compounds were degraded after light
364 irradiation (cf. blue spheres in zone 5; Fig. 5), implying that lignin-like P-containing
365 formula compounds were not completely inert and their reactivity could be related to
366 their molecular structure. In contrast, lignin-like P-containing formula compounds with
367 high O/C (pink spheres in Fig. 5) were produced after light irradiation. These results
368 suggest that lignin-like P-containing formula compounds with a low oxygen content
369 are more photosensitive than those with a high oxygen content. The relationship
370 between the light sensitivity of lignin-like P-containing formula compounds and their
371 molecular structures should be further investigated in future studies. The generated P-
372 containing formulas were mainly protein- and carbohydrate-like P-containing formula
373 compounds, i.e., biolabile compounds and semibiolabile compounds freshly generated
374 in surface waters (Chen et al., 2014; Wagner et al., 2015). In brief, P-containing
375 formulas generated after light irradiation have a high oxygen content, high saturation,
376 and low aromaticity.

377 **3.3. Role of ROS**

378 ROS play an important role in the element cycle of aquatic systems (Cory et al.,
379 2010). Particularly, $^3\text{CDOM}^*$, $\bullet\text{OH}$, H_2O_2 , $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$ are associated with the
380 transformation of OM in water under light irradiation (Li et al., 2015; McNeill and
381 Canonica, 2016; Mostafa and Rosario-Ortiz, 2013; Page et al., 2011; Wang et al., 2021;

382 Zhang et al., 2014). To assess the effects of ROS on POM photodegradation, a series of
383 ROS capture experiments were performed. As shown in Fig. 7, the release of DIP
384 decreased to varying degrees after adding various free-radical scavengers. After adding
385 TMP (a $^3\text{CDOM}^*$ scavenger), the release of DIP decreased by 59.2%. After adding IPA
386 (an $\bullet\text{OH}$ scavenger) and CAT (an H_2O_2 scavenger), the release of DIP decreased by
387 38.8% and 32.6%, respectively. The order of contribution of each ROS was as follows:
388 $^3\text{CDOM}^* > \bullet\text{OH} > \text{H}_2\text{O}_2 > ^1\text{O}_2 > \text{O}_2^{\bullet-}$. Fig. S9 presents the time evolution of H_2O_2 , $\text{O}_2^{\bullet-}$,
389 PBA, FFA (a probe of $^1\text{O}_2$), and TMP (a probe of $^3\text{CDOM}^*$). During dark treatment,
390 there was no obvious transformation of probe molecules, which was observed in
391 ultrapure water (especially for FFA and TMP). The steady-state concentrations and
392 formation rates of $^1\text{O}_2$ and $^3\text{CDOM}^*$ are summarized in Table S6. The steady-state
393 concentrations and formation rates were 1.51×10^{-13} M and 0.76×10^{-7} M/s,
394 respectively, for $^3\text{CDOM}^*$ and 0.43×10^{-12} M and 0.11×10^{-6} M/s, respectively, for $^1\text{O}_2$
395 in suspension, being much lower than those in filtered lake water. This indicates that
396 the presence of particles hinders the production of $^1\text{O}_2$ and $^3\text{CDOM}^*$ or that the
397 generated $^1\text{O}_2$ and $^3\text{CDOM}^*$ are rapidly absorbed by particles. However, opposite
398 results were observed for $\bullet\text{OH}$. The accumulated $\bullet\text{OH}$ content gradually increased with
399 an increase in illumination time, and those in suspension were higher than those in
400 filtered lake water. Thus, $\bullet\text{OH}$ plays an important role in the photorelease of DIP.
401 Previous studies have revealed that both DOP and particulate organic phosphorus (POP)
402 can be photolyzed to release DIP (Li et al., 2022; Zhang et al., 2019). The release of
403 DIP from DOP is caused by the cleavage of P-O bonds by $\bullet\text{OH}$ (Zhao et al., 2018).

404 During the photodegradation of POM, we found that the release of DIP was
405 accompanied by an increase in DOP concentration (Fig. S4). Hence, it can be inferred
406 that POP in POM is first converted to DOP and DOP is then oxidized to produce DIP.

407 In general, $\bullet\text{OH}$ is the main ROS affecting the photochemical transformation of
408 OM in water (Goldstone et al., 2002). We previously found that the photolytic release
409 of P in water significantly decreased after adding an $\bullet\text{OH}$ scavenger (Li et al., 2017b).
410 However, this phenomenon is different in lakes with different trophic states. In
411 mesotrophic lakes, NO_3^- is the main contributor of $\bullet\text{OH}$ in water. With the proliferation
412 of lake eutrophication, dissolved organic matter (DOM) gradually becomes the main
413 contributor of $\bullet\text{OH}$ in water bodies (Guo et al., 2020). Lake Nanhu, selected in this
414 experiment, is severely affected by eutrophication, and DOM is the main contributor to
415 $\bullet\text{OH}$ generation in this lake. Notably, the photochemical reaction of DOM does not
416 directly generate $\bullet\text{OH}$. Instead, it first generates $^3\text{CDOM}^*$ under light irradiation and
417 then generates $\bullet\text{OH}$, H_2O_2 , $^1\text{O}_2$, and $\text{O}_2^{\bullet-}$ through a series of reactions (Sharpless and
418 Blough, 2014). The addition of TMP cuts off the subsequent reaction process, thereby
419 inhibiting the photolytic release of dissolved phosphate.

420 **3.4 Environmental implications**

421 POM generally exists in various natural aquatic ecosystems, and its source and
422 composition are extremely complex. It can be divided into exogenous and endogenous
423 types. Exogenous POM mainly includes terrestrial plant debris and OM discharged by
424 human activities and carried by rivers; its flux into lakes exhibits great variability.
425 Endogenous POM is mainly produced by the residues of phytoplankton, large aquatic

426 plants, animals, and their metabolites. In previous studies, POM and DOM were mainly
427 distinguished according to their particle size (Azam and Malfatti, 2007; Roulet and
428 Moore, 2006). However, this classification does not fully reflect the chemical
429 characteristics, biological characteristics, and ecological functions. In fact, part of the
430 POM in aquatic ecosystems is relatively stable and difficult to decompose. It hardly
431 participates in the ecological process. In contrast, the other part is very active and has
432 an abnormally rapid turnover rate. This rapid transformation and degradation have an
433 important impact on the distribution pattern of nutrients and the recycling process.
434 However, understanding of the structural composition, degradation rate, and
435 transformation mechanism of POM in aquatic ecosystems is limited, resulting in a lack
436 of important links and basis for objectively describing the eutrophication process and
437 in turn controlling water bloom.

438 In eutrophic shallow lakes, excessive phytoplankton growth results in a large
439 amount of suspended POM. With the growth of phytoplankton, dissolved inorganic
440 nutrients are gradually consumed, and the mineralization and decomposition of POM
441 become an important nutrient compensation source. We found that POM exposed to
442 light irradiation could be photodegraded and DIP could be subsequently released. FT-
443 ICR MS revealed that the average molecular weight of P-containing formulas in POM
444 significantly decreased after light irradiation. P species in POM with lower oxidation
445 degrees and/or unsaturation were preferentially photodegraded, resulting in the
446 generation of species with higher oxidation degrees and more saturation (such as
447 protein- and carbohydrate-like P-containing formula compounds). $^3\text{CDOM}^*$ was

448 chiefly responsible for the photodegradation of POM. With the intensification of lake
449 eutrophication, the easily degradable components of POM and the yield of $^3\text{CDOM}^*$
450 photo induced by DOM increase. The interaction between POM and $^3\text{CDOM}^*$ can lead
451 to the rapid degradation of P species and their transformation into DIP, thereby
452 exacerbating the P transformation rate in a water body. This indicates the importance of
453 focusing on the continuous supply of endogenous P to study eutrophication and control
454 blooms occurring in shallow lakes.

455 **4. Conclusions**

456 This study investigated the mechanism underlying DIP release during POM
457 photodegradation using EEM and FT-ICR MS. POM in suspension was photodegraded
458 and released DIP under light irradiation, and OP in POM participated in the
459 photochemical reactions. The photodegradable P-containing formulas were mainly
460 characterized by a lower oxidation degree and unsaturation. Meanwhile, some new P-
461 containing formula compounds, particularly protein- and carbohydrate-like P-
462 containing formulas that had a high oxygen content and were saturated, were
463 photogenerated. $^3\text{CDOM}^*$ was the main ROS that played an important role in the
464 photodegradation of POM. These results provide new insights into the biogeochemical
465 cycle of POM and P in aquatic ecosystems and may further deepen our understanding
466 of algal blooms in shallow lakes.

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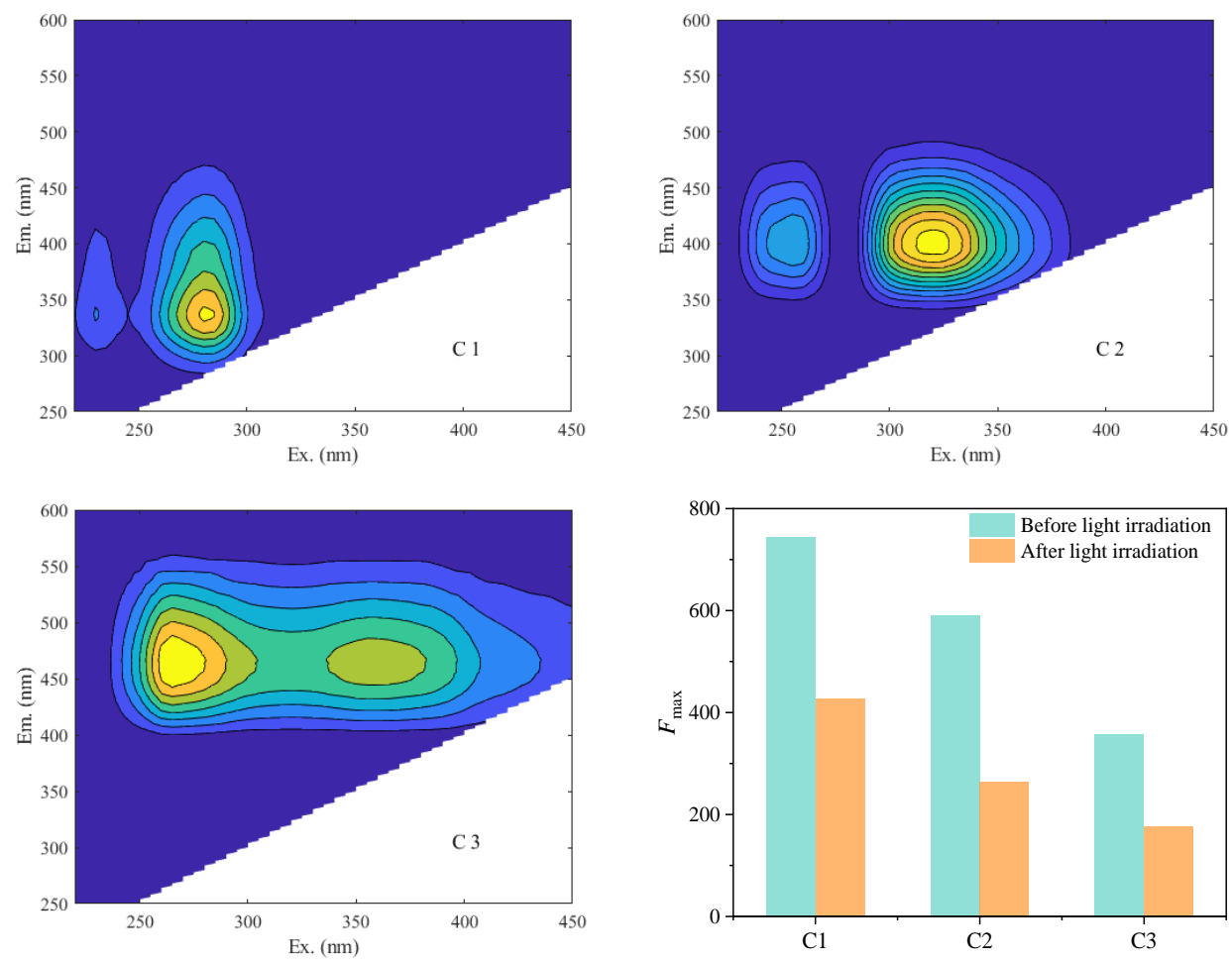
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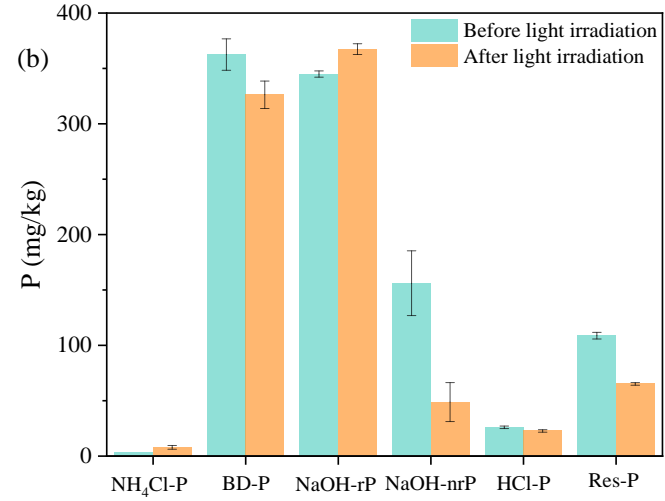
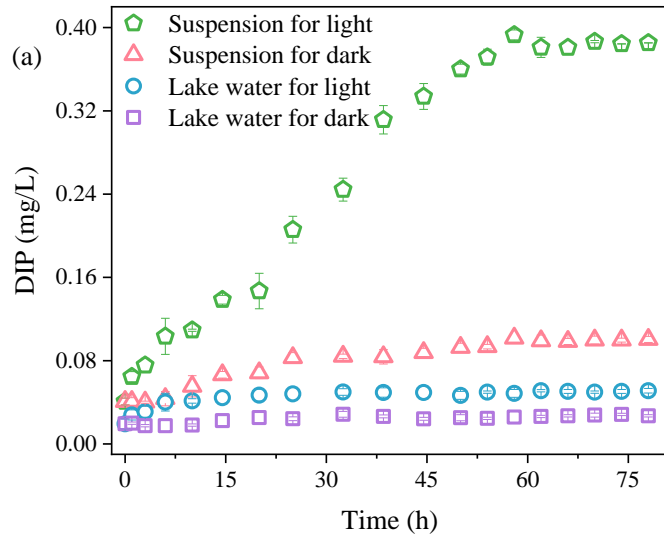
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Fig. 1. The three fluorescent components of POM identified by EEM-PARAFAC modeling (C1-C3, respectively) and their F_{\max} before and after light irradiation.

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7 **Fig. 2.** (a) The concentration changes of DIP in filtered lake water and suspension under light irradiation or dark treatment; (b) Changes of P fractions in

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POM obtained from suspension solution before and after light irradiation.

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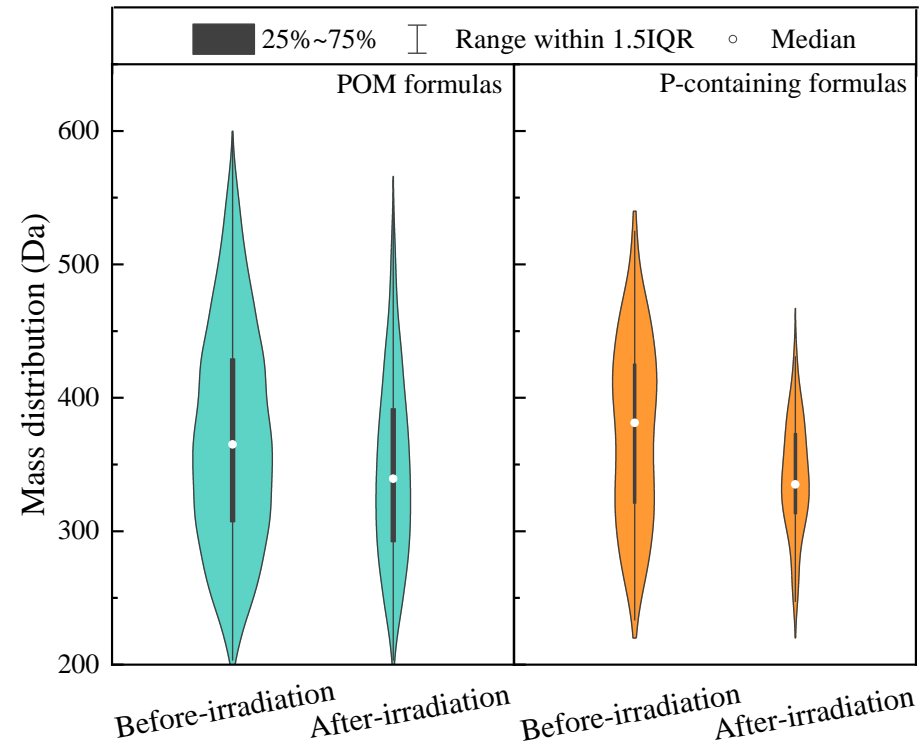
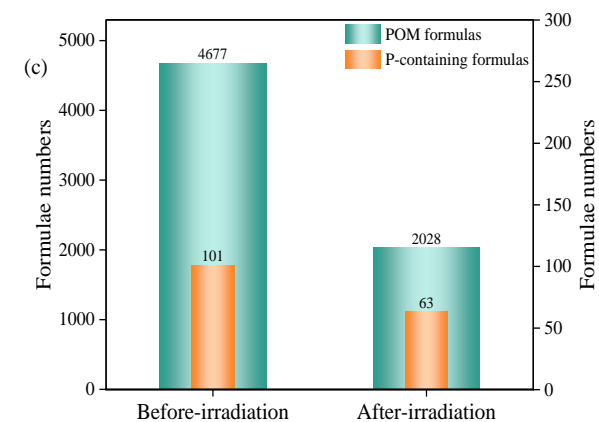
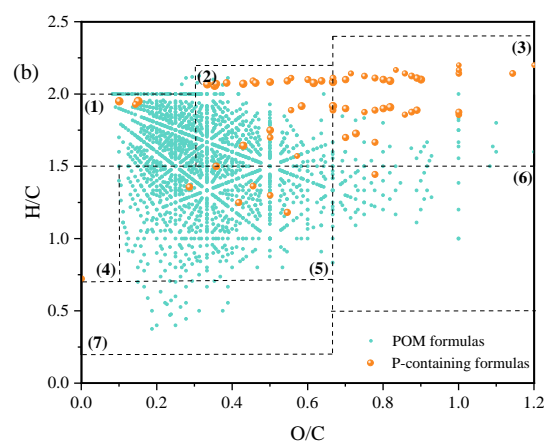
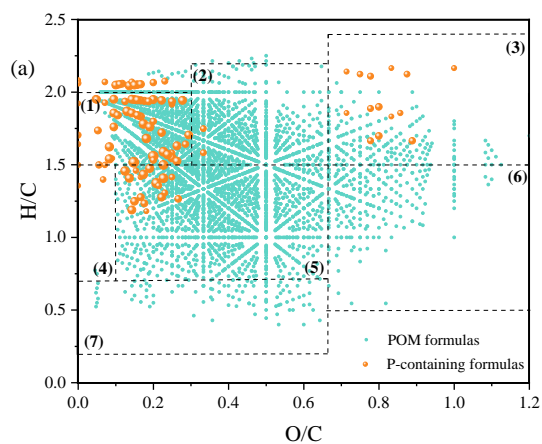


Fig. 3. Mass distributions of POM and P-containing formulas before and after light irradiation

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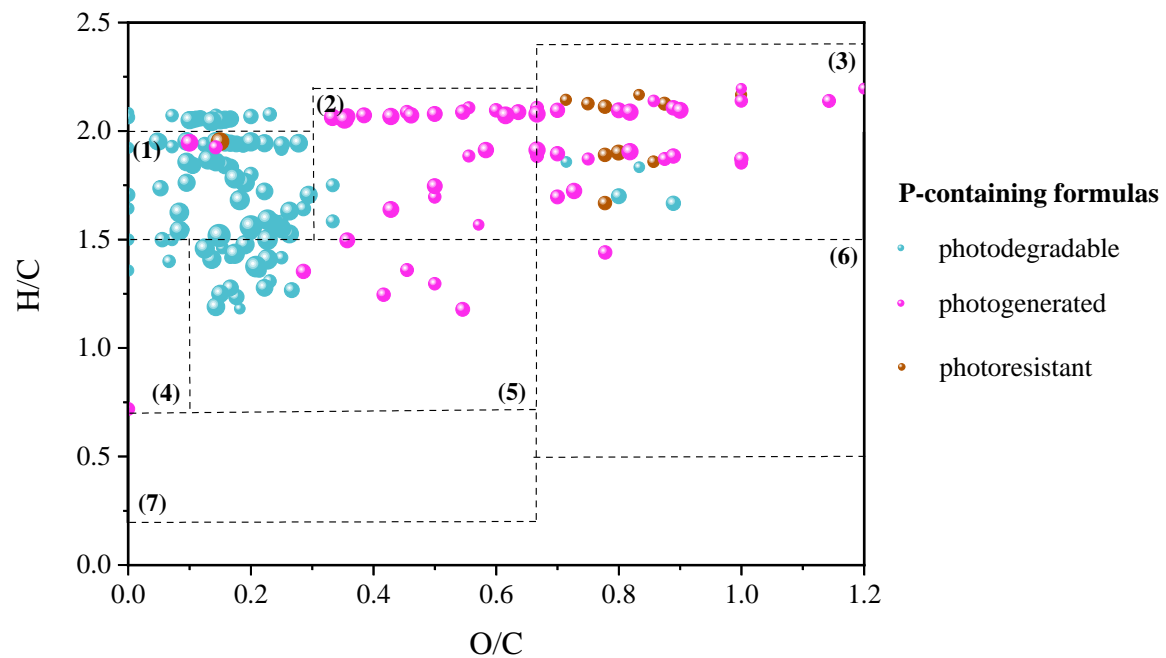


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15 **Fig. 4.** Van Krevelen diagrams from the mass spectra of POM and P-containing formulae before (a) and after (b) light irradiation and their formulae
 16 numbers distribution change (c). The different boxes represent specific compound categories, including: (1) lipids-; (2) proteins-; (3) carbohydrates-; (4)

17 unsaturated hydrocarbons-; (5) lignins-; (6) tannins-, and (7) condensed aromatic structures-like formula compounds. Blue dots represent POM
 18 formulae, and orange spheres represent P-containing formulae. The size of the orange spheres represents the molecular weight of P-containing formulae.

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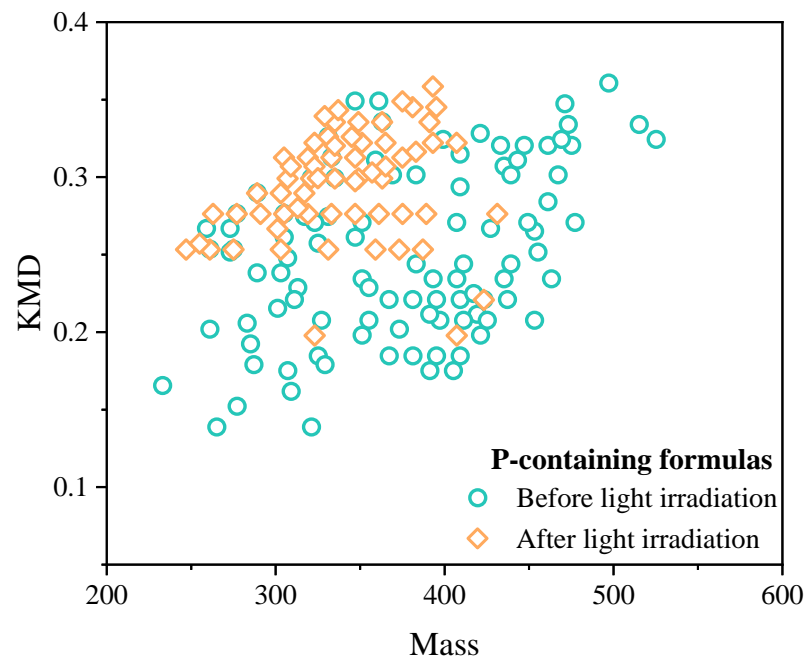


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21 **Fig. 5.** Van Krevelen diagrams of photodegradable, photogenerated, and photoresistant P-containing formulas during POM photodegradation. The size
 22 of the sphere represents the molecular weight of each P-containing formula.

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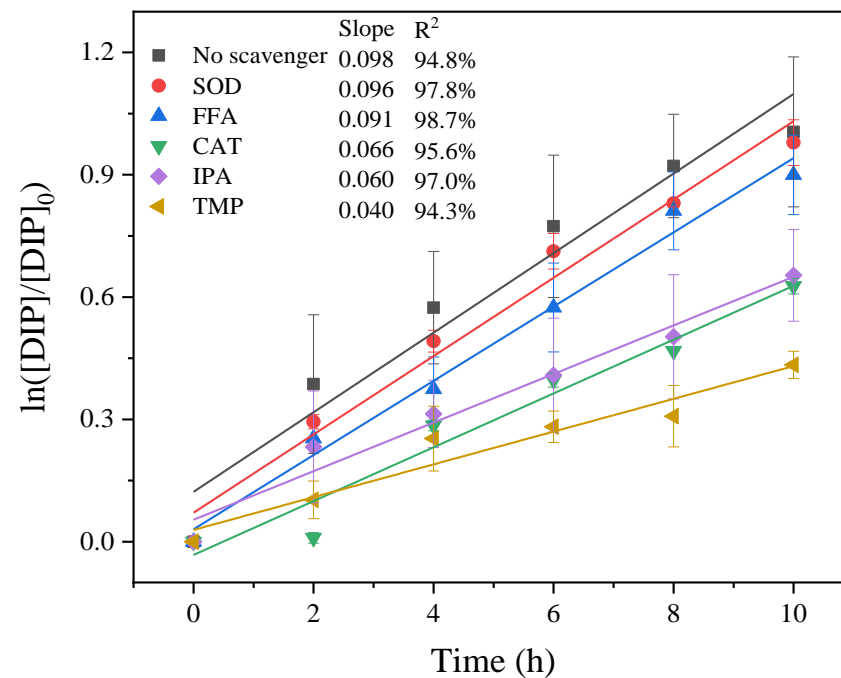
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Fig. 6. Kendrick mass defect (KMD) analysis of P-containing formulas before (a) and after (b) light irradiation.

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31 **Fig. 7.** The inhibition effect of different radical scavengers on the release of DIP during POM photodegradation (SOD for $O_2^{\cdot-}$, FFA for 1O_2 , CAT for

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H_2O_2 , IPA for $\cdot OH$, TMP for $^3CDOM^*$).