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1 **Effect of UVC pre-irradiation on the Suwannee river Natural Organic Matter (SRNOM)**  
2 **photooxidant properties**

3

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14

15 **Abstract :** The present study aimed to investigate the changes in the chemical composition,  
16 and in the optical and photooxidant properties of Suwannee River Natural Organic Matter  
17 (SRNOM) induced by UVC (254 nm) treatment. The extent of the photodegradation was first  
18 assessed by UV-visible/fluorescence spectroscopies and organic carbon analysis. An in-depth  
19 investigation of the chemical changes was also conducted using liquid chromatography-mass  
20 spectrometry and gas chromatography-mass spectrometry after derivatizations. A series of  
21 mono, di and tricarbonyls and mono and dicarboxylic acids in C<sub>1</sub>-C<sub>6</sub> were identified in  
22 samples irradiated from 1 to 4 h. After 3 h of irradiation, carbonyls accounted for 46% of the  
23 organic carbon remaining in solution whereas carboxylic acids represented about 2%. Then,  
24 we investigated the modifications of the photooxidant properties of SRNOM induced by these  
25 chemical changes. At 254 nm, UVC pre-irradiated SRNOM photodegraded glyphosate 29  
26 times faster than original SRNOM and the reaction was fully inhibited by 2-propanol ( $5 \times 10^{-3}$   
27 M). This enhanced photooxidant properties at 254 nm toward glyphosate was therefore  
28 reasonably due to •OH radicals formation, as confirmed by additional ESR measurements. A  
29 mechanism involving a chain reaction was proposed based on independent experiments  
30 conducted on carbonyl compounds, particularly pyruvic acid and acetone. The findings of this  
31 study show that UVC pre-treatment of NOM can enhance the removal of water pollutants and  
32 suggests a possible integration of a NOM pre-activation step in engineered water treatment  
33 systems.

34

35 Key-words: Natural organic matter, carbonyls, hydroperoxides, chain reaction, glyphosate,  
36 •OH radicals

37

38

39

## 40 **Introduction**

41 Natural organic matter (NOM) is a complex mixture of organic compounds formed in  
42 soils, sediments and natural waters as a result of microbial and chemical transformation of  
43 plant tissues and microbial remains and it is an ubiquitous constituent of surface waters and  
44 drinking water supplies. NOM needs to be removed in the process of drinking water  
45 production because it can affect the color and organoleptic parameters of water and it can act  
46 as a carrier of toxic organic compounds [Zoschke et al , 2012 ; Tang et al , 2014]. Under UVC  
47 radiations (200-280 nm), typically used to remove bacterial and chemical contamination  
48 [Sillanpää et al., 2018], NOM undergoes extensive degradation even though complete  
49 mineralization is not usually achieved; the generation of potentially harmful by-products  
50 originating from NOM degradation is a crucial aspect of drinking water production  
51 [Buchanan et al, 2006]. Even though great efforts were put toward a better understanding of  
52 the fate of NOM in UVC treatments [Ike et al, 2019 ; Paul et al, 2012 ; Varanasi et al, 2018 ;  
53 Sarathy et al, 2011 ; Kulovaara et al, 1996; Schmitt-Kopplin et al, 1996 ; Corin et al, 1996 ;  
54 Polewski et al, 2005 ; Lamsal et al, 2011; Rougé et al, 2020], many questions related to the  
55 nature of intermediary photoproducts formed and their photoreactivity remain unanswered  
56 and need to be further investigated.

57 Due to its heterogeneity and chemical complexity, NOM transformation was often  
58 studied by monitoring global parameters using techniques such as absorption or fluorescence  
59 spectroscopy, total organic carbon analysis, <sup>13</sup>C NMR, pyrolysis and gel permeation  
60 chromatography [Ike et al, 2019 ; Paul et al, 2012 ; Hao et al, 2020 ; Sarathy and Mohseni,  
61 2007 ; Fukushima et al, 2001 ; Schmitt-Kopplin et al, 1996 ; Polewski et al, 2005]. These  
62 analytical techniques allowed to assess an overall decrease of NOM UV-visible absorbance,  
63 of aromaticity and of molecular weight during oxidation processes. Several studies focused on  
64 the identification of small molecules, generated from NOM breakdown, by coupling

65 derivatization techniques with liquid chromatography-mass spectrometry (LC-MS) or gas  
66 chromatography-mass spectrometry (GC-MS). Formation of C<sub>1</sub>-C<sub>4</sub> carbonyl compounds and  
67 C<sub>2</sub>-C<sub>5</sub> carboxylic acids, amino acids and alcohols in UVC treatments was reported [Thomson  
68 et al, 2004 ; Agbaba et al, 2016 ; Zhong et al, 2017 ; Corin et al, 1996]. Some of these  
69 photoproducts were also found upon irradiation of NOM with natural or simulated solar-light  
70 ( $\lambda > 290$  nm) [Brinkmann et al, 2003 ; de Bryun et al, 2011 ; Goldstone at al, 2002 ; Kieber et  
71 al, 1990].

72         The presence of NOM in UVC treatments has been generally reported to lower  
73 treatment efficiency due to its ability to scavenge the reactive species generated under  
74 irradiation and/or to absorb photons competitively, therefore decreasing the degradation rate  
75 of target compounds [Wang et al, 2016]. However, NOM is able to generate oxidant species  
76 such as hydroxyl radicals ( $\bullet\text{OH}$ ), singlet oxygen ( $^1\text{O}_2$ ) and triplet excited states ( $^3\text{NOM}^*$ )  
77 under irradiation [Vione et al, 2014] and can also promote the degradation of contaminants  
78 during UVC treatment [Lester et al, 2013]. The photosensitizing properties of NOM may  
79 evolve during the UVC treatment because NOM itself undergoes chemical changes. Yet, to  
80 the best of our knowledge, very few studies investigated the effect of such modifications on  
81 the ability of NOM to generate photooxidants in the course of engineered water treatments.  
82 Treatments of NOM with hypochlorous acid and ozone were reported to increase its capacity  
83 to generate  $^1\text{O}_2$  in simulated solar light due to the possible formation of quinone-like  
84 molecules [Mostafa and Rosario-Ortiz, 2013 ; Leresche et al, 2019] but also to decrease its  
85 capacity to generate  $^3\text{NOM}^*$  due to photosensitizers destruction [Wenk et al, 2015]. On the  
86 other hand, UV/chlorine treatment of NOM at high chlorine dosage was found to increase its  
87 ability to generate  $^3\text{NOM}^*$ ,  $^1\text{O}_2$ , and  $\bullet\text{OH}$ , upon irradiation within the range 290-400 nm  
88 [Zhou et al, 2021]. Again, these effects were proposed to be due to the formation of quinone  
89 and ketone functional groups.

90           The goal of this work was to study the chemical changes of SRNOM under UVC  
91 irradiation and to determine how these changes affect its photodegrading properties. In the  
92 first part, spectral changes of irradiated SRNOM solutions were monitored by UV-visible and  
93 fluorescence spectroscopies while photoproducts were analyzed by derivatization of SRNOM  
94 followed by liquid chromatography coupled to high resolution mass spectrometry (UHPLC-  
95 HRMS) or gas chromatography coupled to mass spectrometry (GC-MS). In the second part,  
96 we studied the effect of the UVC pre-irradiation on the photosensitizing properties of  
97 SRNOM. For the experiments at 254 nm, we chose glyphosate, as a probe molecule, for two  
98 reasons. It is non-absorbant at 254 nm and thus poorly subject to photolysis. Moreover, its  
99 aliphatic and saturated structure makes it difficult to oxidize except by very oxidant species  
100 such as  $\bullet\text{OH}$ . The photooxidant properties of carbonyls at 254 nm was also studied for  
101 comparison. For the experiments at  $\lambda > 300$  nm, we used recommended probe molecules to  
102 compare the formation of  $\bullet\text{OH}$ ,  $^3\text{SRNOM}^*$  and singlet oxygen before and after UVC pre-  
103 irradiation [Rosario-Ortiz and Canonica, 2016].

104

## 105 **Material and methods**

### 106 **Chemicals**

107 SRNOM (2R101N) was purchased from the International Humic Substances Society (IHSS).  
108 Glyphosate (99.7%) and  $\text{H}_2\text{O}_2$  (> 30%) were obtained from Fluka. Methylglyoxal (40% in  
109 weight), pyruvic acid (98%), glycolic acid (98%), acetone (> 99.5%), 2,4,6-trimethylphenol  
110 (TMP, certified reference material), furfuryl alcohol (FFA, analytical grade), terephthalic acid  
111 (98%), hydroxyl-terephthalic acid (97%), 2,4-dinitrophenylhydrazine (DNPH, 97%),  
112 bis(trimethylsilyl)trifluoro-acetamide containing 1% trimethylchlorosilane (BSTFA + 1%  
113 TMCS, 98.5% excluding TMCS),  $\text{NaH}_2\text{PO}_4$  ( $\geq 99.5\%$ ),  $\text{Na}_2\text{HPO}_4$  ( $\geq 99\%$ ), horseradish  
114 peroxidase (52 units per mg of solid), 4-hydroxyphenylacetic acid (98%), 5,5-dimethyl-1-

115 pyrroline-N-oxide (DMPO, > 98%) and catalase (2000-5000 units per mg of protein were  
116 purchased from and Sigma Aldrich. Water was purified by reverse osmosis RIOS 5 and  
117 Synergy, Millipore device, with resistivity 18 MΩ cm and DOC < 0.1 mg L<sup>-1</sup>. All these  
118 chemicals were used as received.

### 119 **UVC pre-irradiation of SRNOM**

120 Briefly, 10 mg of SRNOM were dissolved in 250 ml of purified water to reach a  
121 concentration of 40 mg L<sup>-1</sup>. SRNOM solutions were buffered at pH 7 using phosphate buffers  
122 (10<sup>-3</sup> M) except for experiments conducted to monitor the pH evolution during irradiation or  
123 designed to the detection of carboxylic and hydroxylic intermediates. In these cases, SRNOM  
124 solutions were neutralized to pH = 7 ± 0.2 using freshly prepared NaOH (0.1 M). All the  
125 solutions were stored at 4°C. SRNOM solutions (30 mL) were poured in a quartz glass  
126 cylindrical vessel (2 cm i.d. × 19 cm) and were irradiated in a device equipped with 4  
127 germicidal tubes (253.7 nm, General Electric, 15 W). The photon flux entering the solution,  
128 corresponding to 2.9 × 10<sup>-6</sup> Einstein.L<sup>-1</sup>.s<sup>-1</sup>, was calculated by measuring the rate of  
129 glyphosate loss in the presence of H<sub>2</sub>O<sub>2</sub> (SI-Text 1, Fig SI-1). SRNOM solutions were  
130 irradiated for 1 h, 2 h, 3 h and 4 h in separate experiments and labelled SRNOM<sub>1h</sub>, SRNOM<sub>2h</sub>,  
131 SRNOM<sub>3h</sub>, and SRNOM<sub>4h</sub>, respectively. Irradiated solutions were used for analyses or  
132 sensitizing investigations within the 24 h following irradiation.

133

### 134 **Analysis of original and UVC pre-irradiated SRNOM**

135 UV-visible spectra were recorded on a Varian Cary 3 UV-Vis spectrophotometer.  
136 Fluorescence spectra were recorded using a Perkin Elmer LS 55 Luminescence Spectrometer.  
137 The excitation wavelength was set at 255 nm and the absorbance of solutions was adjusted at  
138 0.10 ± 0.01 at 255 nm by dilution with purified water. The emission spectra were corrected  
139 for the dilution coefficient. Dissolved organic carbon (DOC) was measured using a Shimadzu

140 5050 TOC analyser. Carbonyls contained in SRNOM and irradiated SRNOM were analyzed  
141 by DNPH derivatization [Soman et al, 2008] (SI Text 2). Analyses were performed by ultra-  
142 high performance liquid chromatography (UHPLC) coupled to high resolution mass  
143 spectrometry (HRMS). HRMS was performed on an Orbitrap Q-Exactive (ThermoScientific)  
144 coupled to Ultimate 3000 RSLC (ThermoScientific) UHPLC. Analyses were run in negative  
145 (ESI) electrospray modes. The column was a Kinetec EVO C<sub>18</sub> 100 mm / 2.1 mm, 1.7 μm  
146 (Phenomenex). Details of separation conditions are given in (SI Text 3). Molecular formulas  
147 were obtained setting the difference between experimental and accurate masses to ≤ 5 ppm  
148 while structures are proposed based on the number of DNPH molecules linked to carbonyls  
149 and on the number of double bonds in the carbonyl (NDB). In several cases, several isomers  
150 are possible and given structures are thus only indicative. Pyruvic acid and methylglyoxal  
151 were used as references to estimate the concentration of the other carbonyls (SI Text 3 and  
152 Fig. SI-2).

153 Carboxylic and hydroxylic intermediates were detected by a method using BSTFA  
154 derivatization (SI Text 4) followed by analysis with gas chromatography/electron impact MS  
155 (GC/EI-MS) [Yu et al, 1998]. Solutions were analyzed on an Agilent 6890N Network gas  
156 chromatograph coupled to a 5973 Network mass selective detector and Agilent 7683B series  
157 injector. Data acquisition and processing and instrument control were performed by Agilent  
158 MSD ChemStation software. Separation conditions are described in (SI Text 4). Mass spectra  
159 were scanned between m/z 50 and m/z 500 with the source temperature set at 230°C.  
160 Identification was based on matching query spectra to spectra present in the reference library  
161 (NIST17), with a minimum spectral similarity measure of 95%. Glycolic acid was derivatized  
162 by BSTFA as for SRNOM samples and used as a reference for the quantification of other  
163 compounds.



164 SRNOM and SRNOM<sub>3h</sub> were also analyzed by ionic Chromatography-Mass spectrometry (IC-  
165 MS). Details are given in SI-text 5.

166

### 167 **Sensitizing properties of original and UVC pre-irradiated SRNOM**

168 Glyphosate was used to probe the formation of very oxidant species such as •OH from  
169 original and pre-irradiated SRNOM solutions at 254 nm. The solutions containing glyphosate  
170 ( $10^{-5}$  M) and SRNOM were prepared by adding 25  $\mu$ L of the stock solution of glyphosate ( $10^{-2}$   
171 M) to 10.2 mL of SRNOM ( $40 \text{ mg L}^{-1}$ ) and by adding purified water to reach the final  
172 volume of 25 mL. For SRNOM<sub>3h</sub> solutions, the same spike of glyphosate was added to 25 mL  
173 of non diluted solution. This way, the two solutions showed the same absorbance of 0.34 at  
174 254 nm. Then, 15 mL of each solution were irradiated in the above-described device. 2-  
175 Propanol was used as a quencher of •OH. Glyphosate ( $10^{-5}$  M) was also irradiated in the  
176 presence of acetone ( $10^{-4}$  M), pyruvic acid ( $10^{-4}$  M), H<sub>2</sub>O<sub>2</sub> ( $10^{-5}$  M), acetone ( $10^{-4}$  M) + H<sub>2</sub>O<sub>2</sub>  
177 ( $10^{-5}$  M). Furthermore, acetone ( $10^{-4}$  M) was irradiated alone and in mixture with H<sub>2</sub>O<sub>2</sub> ( $10^{-5}$   
178 and  $10^{-3}$  M). All these experiments were conducted in air-saturated solutions. The effect of  
179 oxygen on the rate of glyphosate photodegradation in the presence of SRNOM<sub>3h</sub> was studied  
180 by saturating the solution with N<sub>2</sub>. Glyphosate concentration was monitored by UHPLC-  
181 HRMS by integrating peak area at  $m/z = 168.0056 (\pm 5 \text{ ppm})$ . AMPA  
182 (aminomethylphosphonic acid) with  $m/z = 110.0002 (\pm 5 \text{ ppm})$  was the only glyphosate  
183 photoproduct detected. Acetone loss and photoproducts formation were monitored by  
184 derivatization with DNPH followed by UHPLC-HRMS analysis. Photodegrading properties  
185 of SRNOM and SRNOM<sub>3h</sub> solutions were also investigated under irradiation between 300 and  
186 400 nm. Both solutions were diluted by a half during preparation of mixtures. Terephthalic  
187 acid ( $2 \times 10^{-5}$  M) was used to probe •OH radicals, 2,4,6-trimethylphenol ( $2 \times 10^{-5}$  M) to probe  
188 <sup>3</sup>SRNOM\* and <sup>3</sup>SRNOM<sub>3h</sub>\* and furfuryl alcohol ( $5.8 \times 10^{-5}$  M) to trap <sup>1</sup>O<sub>2</sub>. Solutions

189 buffered at pH 7 were irradiated in a device equipped with 6 fluorescent tubes emitting  
190 between 300 and 400 nm [Palma et al, 2020]. Pseudo-first-order rate constants of probes  
191 phototransformation were determined by plotting  $\ln(C_t/C_0) = k \times t$ , where  $C_t$  and  $C_0$  are the  
192 probe concentration at time  $t$  and before irradiation. All the experiments were duplicated.

193

#### 194 **Peroxides titration**

195 Peroxides concentration was measured by the spectrofluorimetric quantification method  
196 previously described by Miller and Kester, 1988. Details of the experiments are given in SI-  
197 text 6.

198

#### 199 **ESR experiments**

200 ESR experiments were carried out using a Bruker EMX, 9.8 GHz equipped with a cavity  
201 ER4105DR and a xenon lamp (Xenovia 200 - 900 nm). The ESR spectra were obtained at  
202 room temperature under irradiation inside the cell of the following mixtures : DMPO (25  
203 mM) in the presence of SRNOM ( $20 \text{ mg L}^{-1}$ ), SRNOM<sub>3h</sub> or  $\text{H}_2\text{O}_2$  ( $5 \times 10^{-3}$  or  $10^{-5}$  M).

204

### 205 **Results and discussion**

#### 206 **1. Spectral changes of SRNOM upon 254-nm irradiation**

207 Fig. 1A shows that the SRNOM solution progressively photobleached. The absorbance  
208 at 254 nm declined by 59% and 77% after 3 and 4 h of irradiation, respectively (Table 1). The  
209 reduction of DOC as a function of irradiation time revealed that SRNOM also underwent  
210 substantial mineralization (35% after 4 h) while the specific ultraviolet absorbance (SUVA)  
211 decreased by 42% and 64% after 3 and 4 h of irradiation, respectively, indicating a loss of  
212 unsaturated/aromatic moieties [Weisshar et al, 2003] (Table1). Yet, the spectrum shape (Fig.

213 1B) and the  $E_2 / E_3$  ratio (Table 1) did not change much indicating that photoproducts  
214 negligibly contributed to the absorption and were poorly absorbing compounds.

215 Irradiation also led to a breakdown of fluorescent species in accordance with previous  
216 studies [Patel-Sorrentino et al, 2004]. The fluorescence intensity at the emission maximum  
217 declined by 53% after 3 h of irradiation, and by 68% after 4 h (Fig 1 C). Fig 1D also shows  
218 that the blue part of the fluorescence emission spectra disappeared the fastest leading to  
219 emission spectra red-shifted by 10 - 15 nm or to a band contraction. On the contrary,  
220 treatment of NOM with radicals such as  $\text{SO}_4^{\bullet-}$  [Zhang et al, 2019] or  $\bullet\text{OH}$  [Varanasi et al,  
221 2018] was reported to induce a blue-shift of fluorescence emission spectra attributed to  
222 preferential degradation of high molecular weight moieties into smaller entities. In these  
223 treatments, radicals are expected to react preferentially with biggest macromolecules offering  
224 the largest number of attack sites while in photolytic treatment the reactivity of generated  
225 excited states is the critical factor. Our results suggest that smaller fluorescent entities initially  
226 present in SRNOM or produced in the course of the treatment were more subject to  
227 photodegradation than larger ones. The reasons could be that they were more light absorbing  
228 because more oxidized and/or underwent less desactivation processes than bigger constituents  
229 being less embedded in large structures than these latter.

230

## 231 **2. Carbonyls and carboxylic acids formation upon 254-nm irradiation of SRNOM**

232 Table 2 summarizes the chemicals detected by DNPH or BSTFA derivatization and by  
233 CI/MS in SRNOM before irradiation and after irradiation. Detailed MS data are given in  
234 Figure SI-3, Tables SI-1 to SI-3 and the structures of photoproducts observed in irradiated  
235 samples are shown in Figure 2. In starting SRNOM, we detected 5 carbohydrates in  $\text{C}_5$  and  $\text{C}_6$   
236 (xylose, rhamnose, fucose, glucose and galactose) mentioned in the IHSS web page, along  
237 with 2 monocarboxylated alkanes in  $\text{C}_3$  and  $\text{C}_{18}$  (glyceric and oleic acids) and 3

238 dicarboxylated alkanes in C<sub>6</sub>, C<sub>9</sub> and C<sub>12</sub> (hexanedioic, nonanedioic and dodecanedioic acids)  
239 (Tables 2 and SI-1). Several carbonyls were found, but only as traces.

240 In SRNOM<sub>3h</sub>, none of the carbohydrates observed in SRNOM were found while 11  
241 carboxylated alkanes were detected: 5 monocarboxylated in C<sub>1</sub> (formic acid), C<sub>2</sub> (acetic and  
242 glycolic acid), C<sub>3</sub> (lactic acid) and C<sub>4</sub> (4-aminobutanoic acid), 7 dicarboxylated alkanes in C<sub>2</sub>  
243 (oxalic acid), C<sub>3</sub> (malonic, tartronic, dihydroxymalonic acids), C<sub>4</sub> (butanedioic and malic  
244 acids), C<sub>5</sub> (glutaric acid) and C<sub>6</sub> (tricarballic acid) (Tables 3 and SI-2). In all the irradiated  
245 samples, 16 carbonyls in C<sub>1</sub>-C<sub>5</sub> were detected among them 7 monocarbonyls (formaldehyde,  
246 acetaldehyde, glycolaldehyde, glyoxylic acid), 7 dicarbonyls (glyoxal, methylglyoxal,  
247 butenedial) and 2 tricarbonyls. Some of these compounds were already reported to be  
248 produced by irradiation of natural surface waters or synthetic waters containing NOM with  
249 natural or simulated solar-light, by ozone treatment or by UV-based AOPs of solutions of  
250 humic substances. This is the case for formic, acetic and oxalic acids [Brinkmann et al, 2003 ;  
251 Goldstone et al , 2002], formaldehyde, acetaldehyde, glyoxal and methylglyoxal [Thomson et  
252 al, 2004 ; Agbaba et al, 2016 ; Zhong et al, 2017 ; de Bryun et al, 2011 ; Kieber et al, 1990],  
253 malonic and butanedioic acids [Corin et al, 1996], and pyruvic acid [Thomson et al, 2004 ].

254 The concentration of the different carbonyls after 1, 2, 3 and 4 h of irradiation were  
255 estimated using derivatized methylglyoxal and pyruvic acid (Table SI-4). Figure 3A shows  
256 the concentration profile of the most concentrated ones, i.e. formaldehyde, glyoxylic acid,  
257 pyruvic acid, glyoxal and glycolaldehyde, as a function of irradiation time. The concentration  
258 of formaldehyde and glyoxylic acid was maximum after 2 h of irradiation and then declined  
259 while that of pyruvic acid, glyoxal and glycolaldehyde increased throughout the 4 h of  
260 irradiation. It shows that SRNOM photodegradation still proceeds beyond 4 h although a  
261 significant absorbance decrease at 254 nm.

262 The total pool of C<sub>1</sub>-C<sub>5</sub> carbonyls was estimated by summing the individual  
263 concentrations. Figure 3B shows that their cumulative concentration increased during the first  
264 2 h of irradiation to reach the value of  $2.8 \times 10^{-4}$  M. Based on these concentrations and on the  
265 DOC measurements, the mass percentage of carbon atoms contained in the detected carbonyls  
266 could be calculated using Eq 1. This percentage was maximum after 3 h of irradiation where it  
267 reached 46% (Figure 3B). This high value demonstrates the very important contribution of  
268 C<sub>1</sub>-C<sub>5</sub> carbonyls to the pool of photoproducts. As most of these compounds poorly absorbed  
269 below 300 nm, their high concentration explains the unchanged spectrum shape following  
270 irradiation.

271

$$272 \quad \text{Mass percentage}_t = \frac{\sum_{i=1}^{i=n} [c_i]_t \times M_i}{\text{DOC}_t} \quad \text{Eq 1}$$

273 where  $[c_i]_t$  and  $M_i$  are the concentration at time t and the molecular mass of carbonyl i, and  
274  $\text{DOC}_t$  is the organic carbon content in the solution at time t.

275 The concentration of carboxylic acids detected in SRNOM<sub>3h</sub> are shown in Table SI-5.  
276 In general, BSTFA-GC-MS and CI-MS analyses gave consistent results regarding the  
277 concentration estimations. BSTFA-GC-MS was however less performant than CI-MS in the  
278 analysis of compounds containing 2 or 3 CO<sub>2</sub>H or OH functions such as tartronic,  
279 dihydroxymalonic acid, oxalic acid and tricarballylic acids. The difficulty to solubilize  
280 lyophilized SRNOM<sub>3h</sub> in acetonitrile to conduct the BSTFA derivatization or a partial  
281 derivatization of these compounds probably explain these discrepancies. Malic, oxalic,  
282 butanedioic, glycolic, and malonic acids were the most concentrated acids. However, their  
283 concentration in SRNOM<sub>3h</sub> that laid below  $2.8 \times 10^{-6}$  M, were much lower than those of  
284 carbonyls. Eq 1 allowed to determine that the detected carboxylic acids contained only 2% in  
285 mass of the SRNOM<sub>3H</sub> carbon atoms.

286 Nitrate ions were also detected by CI-MS in SRNOM at a level of  $2.9 \times 10^{-6}$  M, but  
287 not in SRNOM<sub>3h</sub>.

288 The detection of all these compounds suggests that the photodegradation of SRNOM  
289 under UVC resulted from a complex set of reactions involving the direct photolysis of  
290 SRNOM constituents as well as their oxidation by the radicals generated in the course of the  
291 irradiation. Many radicals such as R•, RO•, RO<sub>2</sub>•, HO<sub>2</sub>•/O<sub>2</sub>• and •OH can be formed by C-C,  
292 C-O, and O-O bond cleavage, phenyl-O<sup>-</sup> and RCO<sub>2</sub><sup>-</sup> photoionization, addition of oxygen on  
293 radicals and various radical attacks. Once formed, these radicals could contribute to further  
294 degradation of SRNOM constituents and of their by-products. Among them, •OH radical is  
295 likely to play a significant role for several reasons. It is the most oxidant species able to react  
296 with a wide variety of chemicals by addition on double bonds or by H atom abstraction  
297 [Buxton et al, 1988]. NOM was shown to generate •OH radicals [Vaughan and Blough, 1998 ;  
298 Page et al, 2011; McKay et al, 2015 ; Gan et al, 2008 ; Sun et al, 2015 ; Dong et al, 2012 ;  
299 Aguer and Richard, 1999] under irradiation. In reactions where •OH radicals are purposely  
300 produced [Varanasi et al, 2018] the oxidation degree of photoproducts, given by the O/C ratio,  
301 is generally high (1-2), as observed here. Last, the photolysis of chlorosalicylic acid, that was  
302 proposed to occur via the intermediary formation of •OH radicals [Tafer et al, 2016], yielded  
303 glycolic, lactic, and butanedioic acids, acetaldehyde, glycoaldehyde, methylglyoxal, C<sub>4</sub>H<sub>4</sub>O<sub>3</sub>,  
304 and C<sub>3</sub>O<sub>3</sub>H<sub>2</sub> that were also detected in the present work.

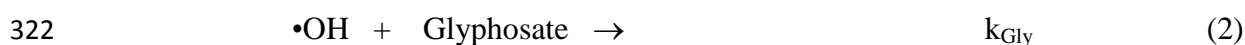
305

### 306 **3. Effect of SRNOM pre-irradiation on the oxidant properties at 254 nm**

307 In order to explore the photooxidant properties of pre-irradiated SRNOM, we chose  
308 glyphosate as a chemical probe. We first checked that it is photostable when irradiated in our  
309 device ( $k < 2 \times 10^{-4} \text{ min}^{-1}$ , Table 3). For these experiments, we selected SRNOM<sub>3h</sub> that  
310 showed the highest concentration of intermediary carbonyl compounds ( $2.4 \times 10^{-4}$  M) and

311 SRNOM and SRNOM<sub>3h</sub> were tested at the same absorbance at 254 nm (0.34). In the presence  
 312 of SRNOM, glyphosate (10<sup>-5</sup> M) disappeared with a rate constant k of 0.0013 ± 0.0002 min<sup>-1</sup>  
 313 in air-saturated solution (Figure 4A and Table 3). Making the hypothesis that the reaction was  
 314 due to the reaction of glyphosate with •OH radicals, we used this rate constant to estimate the  
 315 quantum yield of •OH radicals formation by SRNOM ( $\Phi_{OH}^{SRNOM}$ ) in the first stages of the  
 316 reaction. Once formed by process 1, •OH radicals react with glyphosate ( $k_{gly} = (3.37 \pm 0.10) \times$   
 317  $10^7 \text{ M}^{-1} \text{ s}^{-1}$ , Vidal et al, 2015) (process 2) and with SRNOM (process 3). We took for  $k_{SRNOM}$   
 318 the value of  $1.6 \times 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$  reported in the literature for Suwannee river fulvic acid  
 319 [Westoffer et al, 2007].

320



324

325 The rate of glyphosate photodegradation ( $R_{Gly}$ ) can be written (SI-Text 7):

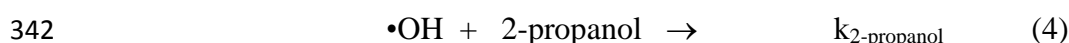
326

$$R_{Gly} = I_0 (1 - 10^{-A_{SRNOM}}) \Phi_{OH}^{SRNOM} \frac{k_{gly} [Gly]}{k_{gly} [Gly] + k_{SRNOM} [SRNOM]} \quad EQ1$$

327

328 where  $I_0 (1 - 10^{-A_{SRNOM}})$  is the rate of light absorption by SRNOM. As SRNOM was diluted  
 329 2.44 fold to reach the same absorbance at 254 nm as SRNOM<sub>3h</sub>, [SRNOM] was equal to 6.35  
 330 mgC L<sup>-1</sup> or 0.529 mM<sub>C</sub><sup>-1</sup>, taking 12 for the molar mass of carbon. In these conditions, one  
 331 gets that glyphosate trapped 0.38% of •OH radicals and that  $\Phi_{OH}^{SRNOM}$  was equal to 0.024;  
 332 this value is in the range of that reported by Lester et al (2013) at 254 nm (0.047).

333 In the presence of SRNOM<sub>3h</sub> and in air-saturated solution, glyphosate disappeared  
 334 much faster than in the presence of SRNOM (Figure 4A) with  $k = 0.038 \pm 0.004 \text{ min}^{-1}$  (Table  
 335 3). In N<sub>2</sub>-purged SRNOM<sub>3h</sub> solution, the glyphosate photodegradation rate was significantly  
 336 reduced compared to the one conducted in air-saturated medium ( $k = 0.002 \pm 0.002 \text{ min}^{-1}$  in  
 337 the first 10 min of the reaction, Figure 4A, Table 3) demonstrating the important role played  
 338 by oxygen in the reaction. Moreover, we irradiated glyphosate and SRNOM<sub>3h</sub> in the presence  
 339 of 2-propanol to determine whether •OH radicals were involved in the loss of glyphosate.  
 340 Using  $k_{2\text{-propanol}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  [Buxton et al, 1998] for the bimolecular rate constant of  
 341 reaction between •OH and 2-propanol :



343 we added  $5 \times 10^{-3} \text{ M}$  of 2-propanol expecting an inhibition of the reaction > 90% based on  
 344  $k_{\text{SRNOM}_{3h}}[\text{SRNOM}_{3h}] \sim 9 \times 10^4 \text{ s}^{-1}$ , as for SRNOM. The inhibition was of 90% (Figure 4A,  
 345 Table 3) in accordance with a significant contribution of •OH.

346 Spin trap experiments using DMPO as the spin-trapping reagent were also conducted  
 347 to confirm the formation of •OH radicals. Figure 5 shows that the four-line signal with an  
 348 intensity ratio 1:2:2:1 characteristic of the DMPO-OH• adduct was not detected when DMPO  
 349 was irradiated in the presence of SRNOM (plot a) or H<sub>2</sub>O<sub>2</sub> ( $10^{-5}$ ) (plot c) while it was  
 350 observed with SRNOM<sub>3h</sub> (plot b) and H<sub>2</sub>O<sub>2</sub> ( $5 \times 10^{-3} \text{ M}$ ) (plot d). Again, this result is in line  
 351 with the production of •OH radicals upon irradiation of SRNOM<sub>3h</sub> in UVC.

352 Postulating that the disappearance of glyphosate was only due to the reaction with  
 353 •OH, we made the same calculation for SRNOM<sub>3h</sub> as for SRNOM, after having replaced  
 354 processes 1 and 2 by processes 1' and 3' respectively:





358

359 and substituting SRNOM by SRNOM<sub>3h</sub> in EQ1. The TOC analyses showed that SRNOM<sub>3h</sub>  
360 had a DOC content of 10.9 mgC L<sup>-1</sup> or 0.907 mM<sub>C</sub><sup>-1</sup> (Table 1). To estimate the percentage of  
361 •OH radicals reacting with glyphosate in SRNOM<sub>3h</sub> solution, we also need to know the value  
362 of k<sub>SRNOM3h</sub>. Since SRNOM<sub>3h</sub> is much less aromatic than SRNOM, and •OH radicals react  
363 more easily with aromatic or conjugated structures than with saturated ones, k<sub>SRNOM3h</sub> is  
364 possibly smaller than k<sub>SRNOM</sub>. Postulating that the rate constant decrease may parallel the  
365 absorbance decrease at 254 nm, we opted for k<sub>SRNOM3h</sub> = (0.7 ± 0.3) × 10<sup>8</sup> M<sub>C</sub><sup>-1</sup> s<sup>-1</sup>. From this  
366 value, the percentage of •OH radicals trapped by glyphosate in SRNOM<sub>3h</sub> solution would lay  
367 between 0.3 and 0.8 % and Φ<sub>OH</sub><sup>SRNOM3h</sup> would be comprised between 0.21 and 0.55, a value  
368 between 10 and 20 times higher than that found for Φ<sub>OH</sub><sup>SRNOM</sup>. This value must be considered  
369 as a maximal value and would be lower if radicals other than •OH also contributed to the  
370 degradation of glyphosate. To better understand the enhancing effect of the pre-irradiation on  
371 the photooxidant properties of SRNOM, we conducted additional experiments and tested  
372 potential candidates for their ability to photodegrade glyphosate.

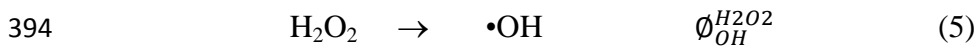
373

#### 374 **4. Peroxides formation and role of H<sub>2</sub>O<sub>2</sub> in the oxidant properties at 254 nm**

375 Peroxides are sources of •OH radicals through direct photolysis (process 5) or photo-  
376 Fenton reaction and we quantified their formation in our system. Measurements of H<sub>2</sub>O<sub>2</sub> and  
377 RO<sub>2</sub>H + RO<sub>2</sub>R were performed on SRNOM and SRNOM<sub>3h</sub> irradiated for 30 min (Figure 5).  
378 In SRNOM, H<sub>2</sub>O<sub>2</sub> and RO<sub>2</sub>H + RO<sub>2</sub>R accumulated linearly. After 30 min of irradiation, the  
379 total concentration of H<sub>2</sub>O<sub>2</sub> + RO<sub>2</sub>H + RO<sub>2</sub>R was equal to 16 μM; H<sub>2</sub>O<sub>2</sub> was by far the most  
380 abundant species (14.2 μM) while RO<sub>2</sub>H + RO<sub>2</sub>R contributed to the pool of peroxides in a  
381 minor way (1.8 μM). In SRNOM<sub>3h</sub>, the peroxides formation was auto-inhibited, slowing  
382 down after 10 min. The total concentration reached 15.8 μM after 30 min ; H<sub>2</sub>O<sub>2</sub> and RO<sub>2</sub>H +

383 RO<sub>2</sub>R were in equivalent amounts of ~ 8.0 μM. The formation of H<sub>2</sub>O<sub>2</sub> in the photolysis of  
 384 NOM is well documented in the literature [Garg et al., 2011]. It is formed by dimutation of  
 385 O<sub>2</sub><sup>-</sup> that arises from reduction of dissolved O<sub>2</sub>. Peroxides and hydroperoxides are generated  
 386 after the reaction of R<sup>•</sup> radicals with dissolved O<sub>2</sub> to yield RO<sub>2</sub><sup>•</sup> and the reaction of these  
 387 peroxy radicals with O<sub>2</sub><sup>-</sup>/HO<sub>2</sub><sup>•</sup> [Sun et al., 2021].

388 To determine the contribution of H<sub>2</sub>O<sub>2</sub> to the formation of •OH via process (5), we  
 389 proceeded as follows. We first measured R<sub>Gly</sub> in the presence of H<sub>2</sub>O<sub>2</sub> (10<sup>-5</sup> M) alone. The  
 390 value of 1.5 × 10<sup>-9</sup> M<sup>-1</sup> s<sup>-1</sup> allowed us to check that glyphosate reacted with •OH and to  
 391 measure the photon flux I<sub>0</sub> in the irradiation device (SI-Text 1). Then, we calculated R<sub>Gly</sub><sup>H2O2</sup>  
 392 in SRNOM solution using Eq 2, supposing that the photolysis of H<sub>2</sub>O<sub>2</sub> produced during the  
 393 irradiation of SRNOM was the only source of •OH through process 5 (SI-Text 5).



395

$$R_{\text{Gly}}^{\text{H}_2\text{O}_2} = I_{\alpha, \text{H}_2\text{O}_2}^{\text{SRNOM}} \Phi_{\text{OH}}^{\text{H}_2\text{O}_2} \frac{k_{\text{gly}} [\text{Gly}]}{k_{\text{gly}} [\text{Gly}] + k_{\text{SRNOM}} [\text{SRNOM}] + k_{\text{H}_2\text{O}_2} [\text{H}_2\text{O}_2]} \quad \text{EQ2}$$

396

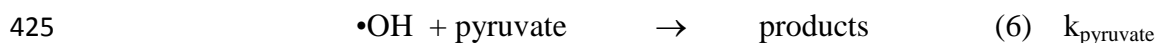
397 Taking [H<sub>2</sub>O<sub>2</sub>] = 14 μM (corresponding to the highest value reached for SRNOM), ε<sub>H2O2</sub> =  
 398 19.6 M<sup>-1</sup> cm<sup>-1</sup> at 254 nm, A<sub>254</sub> = 0.34 for SRNOM and ℓ = 2, we calculated I<sub>α, H2O2</sub><sup>SRNOM</sup> using the  
 399 Beer-Lamber law for a mixture (SI-Text 8). Then, taking k<sub>H2O2</sub> = 2.7 × 10<sup>7</sup> M<sup>-1</sup>.s<sup>-1</sup> [Stephan et  
 400 al, 1996], we got that glyphosate trapped 0.38% of •OH and using Φ<sub>OH</sub><sup>H2O2</sup> = 1 [Yu and  
 401 Barker, 2003], we finally obtained R<sub>Gly</sub><sup>H2O2</sup> = 7.0 × 10<sup>-12</sup> M s<sup>-1</sup>. In the case of SRNOM<sub>3h</sub>, we  
 402 took [H<sub>2</sub>O<sub>2</sub>] = 8 μM and the same calculation led to R<sub>Gly</sub><sup>H2O2</sup> = (3.0-9.0) × 10<sup>-12</sup> M s<sup>-1</sup>. Both  
 403 values are very small compared to the experimental values 2.2 × 10<sup>-10</sup> M s<sup>-1</sup> and 6.5 × 10<sup>-9</sup> M  
 404 s<sup>-1</sup> respectively measured for SRNOM and SRNOM<sub>3h</sub> and it can be concluded that the  
 405 photochemical decomposition of titrated hydroperoxides negligibly contributed to the

406 oxidation of glyphosate. Spontaneous decomposition of unstable hydroperoxides into RO•  
407 and •OH might be an alternative source of •OH radicals. This was considered by Badiali et al  
408 (2015) and Krapf et al (2016) in their studies on secondary organic aerosols.

409

## 410 **5. Role of carbonyls in the photooxidant properties at 254 nm**

411 Given the high concentration of carbonyls detected in SRNOM<sub>3h</sub> and the known  
412 potential of these chemicals as sensitizers, we tested if they could induce the transformation of  
413 glyphosate at 254 nm. We first tested pyruvic acid since this compound had been previously  
414 detected in our irradiated SRNOM samples. In the presence of this ketoacid ( $10^{-4}$  M), in pH 7  
415 buffered solutions, glyphosate ( $10^{-5}$  M) disappeared with an apparent first order rate constant  
416 equal to  $0.021 \pm 0.002 \text{ min}^{-1}$  (Figure 6A, Table 3). Pyruvate was also photodegraded and the  
417 reaction auto-accelerated. During the first 6 min of irradiation, only  $1.8 \times 10^{-6}$  M of pyruvate  
418 were transformed against  $3.1 \times 10^{-5}$  M between 6 and 30 min (Figure 6B). The rate of  
419 pyruvate loss,  $R_{\text{pyruvate}}$ , in the second part of the curve was equal to  $2.1 \times 10^{-8} \text{ M s}^{-1}$ , and  $R_{\text{Gly}}$   
420 to  $3.5 \times 10^{-9} \text{ M s}^{-1}$ . The experiment was repeated in the presence of 2-propanol added to trap  
421 •OH radicals. The concentration  $10^{-4}$  M was chosen for 2-propanol for a theoretical trapping  
422 of more than 95% based on  $k_{\text{pyruvate acid}} = 3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (process 6) [Buxton et al, 1998]. After  
423 30 min, the rate of glyphosate loss was reduced by 75% confirming a significant contribution  
424 of •OH in the reaction.



426

427 Although it was not detected in irradiated SRNOM samples, acetone was chosen to  
428 represent monocarbonyls because it is a simple molecule, it can be purchased in high purity, it  
429 was already studied and its quantum yield of photolysis is known ( $\Phi_{\text{acetone}} = 0.061$  at 270 nm,  
430 Anpo and Kubokawa, 1977). At  $10^{-4}$  M, a concentration falling within the range of that found

431 for intermediary carbonyls, acetone increased the rate of glyphosate photodegradation and the  
 432 reaction was also auto-accelerated (Figure 6A, Table 3). During the first 10 min of reaction,  
 433 an averaged  $k = 0.002 \pm 0.001 \text{ min}^{-1}$  was obtained while, between 10 and 30 min, we  
 434 measured  $k = 0.024 \pm 0.003 \text{ min}^{-1}$ . In parallel, the decay of acetone was monitored by  
 435 UHPLC-HRMS after DNPH derivatization. Acetone also disappeared by an autoaccelerated  
 436 reaction (Figure 6B). Between 0 and 10 min, the loss of acetone was lower than 5%  
 437 corresponding to a rate of acetone photodegradation ( $R_{\text{acetone}} < 0.9 \times 10^{-8} \text{ M s}^{-1}$  while,  
 438 between 10 and 40 min, acetone disappeared by 43% and  $R_{\text{acetone}}$  was equal to  $2.4 \times 10^{-8} \text{ M s}^{-1}$   
 439 (Table 3). During this reaction  $\text{H}_2\text{O}_2$  was formed (Figure 6B). The  $\text{H}_2\text{O}_2$  production was of 2  
 440  $\mu\text{M}$  between 0 and 10 min and 10  $\mu\text{M}$  between 10 and 30 min which mirrored the  
 441 autoaccelerated decrease of glyphosate and acetone. In the presence of 2-propanol ( $10^{-4} \text{ M}$ )  
 442 and acetone ( $10^{-4} \text{ M}$ ), glyphosate disappeared by 10% instead of 42% in the absence of 2-  
 443 propanol after 30 min of irradiation (Figure 6A, Table 3) confirming again a significant  
 444 contribution of  $\bullet\text{OH}$  in the reaction (75%).

445 Acetone was also irradiated alone to check that the observed auto-acceleration was not  
 446 due to the presence of glyphosate. At  $2.4 \times 10^{-4} \text{ M}$ , acetone also disappeared in an auto-  
 447 accelerated reaction with  $R_{\text{acetone}} < 0.9 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$  between 0-10 min and  $R_{\text{acetone}} = 3.9 \times 10^{-8}$   
 448  $\text{M}^{-1} \text{ s}^{-1}$  between 10-30 min (Table 3). The photoproducts were pyruvic acid, methyl glyoxal,  
 449 hydroxyacetone, formadehyde as described by Stephan and Bolton (1999) when they studied  
 450 the photolysis of acetone in the presence of  $\text{H}_2\text{O}_2$  at 254 nm. Using the quantum yield of  
 451 acetone photodegradation in diluted solutions (0.061), and  $\epsilon_{\text{acetone}} = 16 \text{ M}^{-1} \text{ cm}^{-1}$  at 254 nm, it  
 452 is possible to calculate the rate of acetone photodegradation by direct photolysis  
 453  $R_{\text{acetone}}^{dp}$  using EQ3:

454

$$R_{\text{acetone}}^{dp} = I_0 \left(1 - 10^{-A_{\text{acetone}}}\right) \phi_{\text{acetone}} \quad \text{EQ3}$$

455

456 For [acetone]=  $10^{-4}$  M, one gets  $R_{acetone}^{dp} = 1.3 \times 10^{-9} \text{ M s}^{-1}$  and for [acetone]=  $2.4 \times 10^{-4}$  M  
457  $R_{acetone}^{dp} = 3.1 \times 10^{-9} \text{ s}^{-1}$ . These values are consistent with the ones obtained between 0 and  
458 10 min ( $< 9 \times 10^{-9} \text{ M s}^{-1}$ ), and one can conclude that  $R_{acetone}^{dp}$  being negligible behind  $R_{acetone}$   
459 measured in the second part of the curves, other reactions should take place.

460 An autoaccelerated reaction is generally due to the accumulation of key intermediates.  
461 Here, the intermediary chemicals were the acetone photoproducts and peroxides, among  
462 which,  $\text{H}_2\text{O}_2$ . We therefore studied the effect of  $\text{H}_2\text{O}_2$ , used a hydroperoxide model, at the  
463 concentration of  $10^{-5}$  and  $10^{-3}$  M on the photodegradation of acetone ( $2.4 \times 10^{-4}$  M). The  
464 photodegradation of acetone was fast till the very beginning of the irradiation ( $R_{acetone} = 3.5 \times$   
465  $10^{-8}$  and  $1.8 \times 10^{-7} \text{ M s}^{-1}$ , respectively, Table 3) and no auto-accelerating effect was observed.  
466 In this mixture, acetone can disappear by reaction with  $\bullet\text{OH}$  produced from  $\text{H}_2\text{O}_2$  photolysis  
467 (process 7,  $k_{acetone} = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , Buxton et al, 1998). Process 8 is a potential competing  
468 pathway of  $\bullet\text{OH}$  disappearance ( $k_{\text{H}_2\text{O}_2} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  Buxton et al, 1998).

469



472

473 For  $[\text{H}_2\text{O}_2] = 10^{-3}$  M and  $[\text{acetone}] = 2.4 \times 10^{-4}$  M, process 8 was expected to significantly  
474 reduce the percentage of  $\bullet\text{OH}$  radicals trapped by acetone. Taking into account that acetone  
475 should trap about 50% of  $\bullet\text{OH}$ , one obtains  $R_{acetone} = 1.3 \times 10^{-7} \text{ M.s}^{-1}$  against  $1.8 \times 10^{-7} \text{ M s}^{-1}$   
476 measured experimentally. For  $[\text{H}_2\text{O}_2] = 10^{-5}$  M and  $[\text{acetone}] = 2.4 \times 10^{-4}$  M, process 8 was  
477 negligible, and acetone was expected to trap all the  $\bullet\text{OH}$  radicals produced by  $\text{H}_2\text{O}_2$   
478 photolysis. Its rate of decay through process 7 ( $R_{acetone}^{\text{OH}}$ ) was equal to  $2.6 \times 10^{-9} \text{ M s}^{-1}$   
479 according to EQ 4.:

$$R_{acetone}^{OH} = I_0 \left( 1 - 10^{-A_{H_2O_2}} \right) \phi_{OH}^{H_2O_2} \quad EQ4$$

480

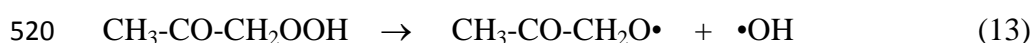
481 This calculated rate accounted for only 6.6% of the measured rate indicating that an additional  
 482 radical source was responsible for acetone degradation. Then, we simultaneously irradiated  
 483 glyphosate ( $10^{-5}$  M),  $H_2O_2$  ( $10^{-5}$  M) and acetone ( $10^{-4}$  M). In this case, the glyphosate  
 484 photodegradation was fast till the beginning of the irradiation ( $k = 0.016 \text{ min}^{-1}$ ) (Figure 6A,  
 485 Table 3) showing that  $H_2O_2$  or other hydroperoxides are important intermediaries in the  
 486 reaction.

487 The results obtained for acetone can be tentatively explained by the chain-reaction  
 488 mechanism shown in Scheme 1. In the classical chain oxidation of a chemical RH bearing a  
 489 labile H atom, the initiator produces the primary radicals (process 9) that start the chain  
 490 through a transfer reaction by generating the radical  $R\cdot$  (process 7). Then  $R\cdot$  produces  $RO_2\cdot$   
 491 by adding  $O_2$  (process 10) and  $RO_2\cdot$  regenerates  $R\cdot$  along to  $RO_2H$  by abstracting of a H from  
 492 RH (process 11). The longer the chain length, the faster the reaction; in fact, when the chain is  
 493 long enough, the rate of the propagation reactions becomes much higher than the rates of  
 494 initiation and of transfer. In our case, the calculated rate of acetone photolysis  $R_{acetone}^{dp}$   
 495 (process 9) was much lower than the experimental rate of acetone photodegradation  
 496 consistently with the involvement of a chain reaction.

497 The irradiation of acetone was expected to yield radicals by  $\alpha$ -cleavage of the triplet  
 498 excited state (process 9) [Pearson, 1963]. The triplet could also abstract a H-atom from  
 499 methyl groups of acetone, however, neither acetone itself nor glyphosate were concentrated  
 500 enough to compete significantly with the cleavage [Anpo and Kubokawa, 1977]. Due to the  
 501 oxidation of these radicals and to the photolysis of the formed hydroperoxides, there should  
 502 be a pool of initiating radicals in the system. The acetyl radical,  $R\cdot$ , formed by process 7  
 503 [Stephan et al, 1996] should easily react with oxygen (process 10) to yield the peroxy radical

504 ROO• [Stephan et al, 1996]. This peroxy radical likely abstracted an H-atom from acetone  
505 (process 11) to regenerate the acetyl radical and produce the hydroperoxide ROOH. The  
506 recombination of two peroxide radicals (process 12) terminated this chain reaction.

507 In this chain reaction, glyphosate might be oxidized by several of the radicals  
508 formed in the complex mixture. However, while the reaction with •OH was evidenced, the  
509 oxidation with the other radicals remains to be demonstrated. If we make the hypothesis that  
510 •OH contributed significantly to the glyphosate degradation, the source of •OH needs to be  
511 explained. Indeed, calculations showed that the photolysis of the different hydroperoxides did  
512 not yield enough radicals to explain the high rate of glyphosate degradation. An alternative  
513 formation of •OH could be the spontaneous decomposition at room temperature of unstable  
514 hydroperoxides, here CH<sub>3</sub>-CO-CH<sub>2</sub>OOH (process 13). According to the works of Badiali et al  
515 (2015) and Krapf et al (2016), the formation of very unstable hydroperoxides is plausible.  
516 Therefore, despite processes 7, 10 and 11 still taking place, the key process became process  
517 13 since it introduced a continuous source of •OH and RO• radicals. Consequently, the rate of  
518 glyphosate degradation increased during the accumulation phase of ROOH, reaching the  
519 maximal value rate when the RO<sub>2</sub>H formation equaled the RO<sub>2</sub>H decomposition.



521 In the case of SRNOM<sub>3h</sub>, carbonyls were present at  $2.4 \times 10^{-4}$  M and hydroperoxides  
522 were potentially generated at a fast rate, therefore making it possible the mechanism already  
523 proposed in the case of acetone to occur. In accordance, ROOH + ROOR were formed along  
524 with H<sub>2</sub>O<sub>2</sub>. In SRNOM<sub>3h</sub> solution, R<sub>gly</sub> was equal to  $6.3 \times 10^{-9}$  M s<sup>-1</sup>. Considering that  
525 glyphosate trapped between 0.3 and 0.8 % of •OH radicals in competition with SRNOM<sub>3H</sub>  
526 constituents, the rate of •OH formation should be comprised between  $\sim 8 \times 10^{-7}$  and  $2 \times 10^{-6}$   
527 M s<sup>-1</sup>. In the model solution containing glyphosate ( $10^{-5}$  M), H<sub>2</sub>O<sub>2</sub> ( $10^{-5}$  M) and acetone ( $10^{-4}$   
528 M), R<sub>gly</sub> was equal to  $2.7 \times 10^{-9}$  M s<sup>-1</sup>. Considering that •OH contributed to the reaction at

529 75% and that glyphosate trapped 3% of •OH in competition with acetone, then the rate of •OH  
530 formation should be equal to  $\sim 7 \times 10^{-8} \text{ M s}^{-1}$ . For acetone ( $2.4 \times 10^{-4} \text{ M}$ ), it might be  $\sim 1.7 \times$   
531  $10^{-7} \text{ M s}^{-1}$ . This value is smaller than that estimated for the SRNOM<sub>3h</sub> solution, and several  
532 explanations of this difference can be proposed: (i) SRNOM<sub>3h</sub> was a much more complex  
533 system than H<sub>2</sub>O<sub>2</sub> + acetone and quantitative results cannot be directly transferable;  
534 furthermore, calculation lays on an hypothetical value of the bimolecular reaction rate  
535 constant of SRNOM<sub>3h</sub> with •OH; (ii) Acetone was chosen as a model compound but among  
536 the carbonyls formed in SRNOM<sub>3h</sub>, some may absorb more than acetone, especially those  
537 bearing double bonds, and/or photodissociate much more easily [Anpo and Kubokawa, 1977];  
538 (iii) SRNOM<sub>3h</sub> also contained chemicals acting probably as better H-donors than acetone and  
539 glyphosate, which should favour process 11 and thus the formation of unstable  
540 hydroperoxides; (iv) Oxidant species other than •OH might contribute to the photodegradation  
541 of glyphosate.

542 In the case of SRNOM,  $R_{\text{Gly}}$  was much higher than  $R_{\text{Gly}}^{\text{H}_2\text{O}_2}$  as for SRNOM<sub>3h</sub>  
543 suggesting that chain reactions might take place as for SRNOM<sub>3H</sub>, although leading to a much  
544 slower production of •OH. Accordingly, the 6-times less formation of ROOR+ROOH from  
545 SRNOM than from SRNOM<sub>3h</sub> suggests that unstable hydroperoxides should be produced in  
546 smaller amounts by SRNOM than by SRNOM<sub>3h</sub>. Spectral measurements showed that  
547 SRNOM is much more aromatic than SRNOM<sub>3h</sub> which constitutes an important difference in  
548 terms of •OH reactions. The •OH radicals are known to add on phenols [Lundquist and  
549 Eriksson, 2000] to finally produce unreactive phenoxyl radicals while they generate radicals  
550 oxidable into hydroperoxides when they abstract hydrogen atoms from aliphatic compounds.  
551 Hence, the presence of carbonyls in SRNOM<sub>3h</sub> could not only favour the formation of radicals  
552 through their photolysis but also constitutes a pool of aliphatic compounds oxidable into  
553 hydroperoxides.



554 AMPA was the main glyphosate photoproduct detected by UHPLC-HRMS (Figure  
555 4B). In the literature, other oxidation products were also detected such as sarcosine [Chen et  
556 al, 2007], not detected in this work. After 30 min of irradiation, the highest yield of AMPA  
557 was measured with H<sub>2</sub>O<sub>2</sub> (66%), followed by SRNOM<sub>3h</sub> (62%), acetone (57%) and pyruvic  
558 acid (38%). Interestingly, when 2-propanol was added to acetone and pyruvate solutions, the  
559 yield of AMPA dropped to 10% and 17%, respectively. The formation of AMPA may be thus  
560 an indirect evidence of the involvement of •OH radicals in the photodegradation.

561

### 562 **5. Effect of SRNOM pre-irradiation on •OH, <sup>1</sup>O<sub>2</sub> and <sup>3</sup>SRNOM\* formation under** 563 **simulated solar light**

564 We also compared the ability of SRNOM and SRNOM<sub>3h</sub> to photoproduce  
565 photooxidants <sup>3</sup>SRNOM\*, <sup>1</sup>O<sub>2</sub> and •OH in simulated solar-light. After the normalization for  
566 light absorption, the rate of 2,4,6-trimethylphenol was found to be 1.5 times higher in SRNOM  
567 than in SRNOM<sub>3h</sub>, in accordance with lower rate of <sup>3</sup>SRNOM\* formation. Therefore,  
568 chromophores yielding <sup>3</sup>SRNOM\* were partly degraded under UVC irradiation. In the case of  
569 <sup>1</sup>O<sub>2</sub> titrated using furfuryl alcohol, we found rates of formation varying by less than 10%  
570 between SRNOM and SRNOM<sub>3h</sub>. At last, results on terephthalic acid used to estimate the rate  
571 of •OH formation showed a higher rate of •OH formation in SRNOM<sub>3h</sub> solution than in  
572 SRNOM solution. Taking  $k_{\text{SRNOM}} = 1.6 \times 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$  and  $k_{\text{SRNOM}_{3h}} = 0.7 \times 10^8 \text{ M}_C^{-1} \text{ s}^{-1}$  for the  
573 bimolecular rate constants of reaction with •OH, we got a rate of •OH formation higher by  
574 40% for SRNOM<sub>3h</sub> solution than for SRNOM solution. This enhancement was much lower  
575 than the one observed at 254 nm with glyphosate. The dependence of the •OH formation  
576 enhancement on the irradiation wavelength supports the hypothesis of the involvement of  
577 poorly conjugated and light absorbing carbonyl compounds in the photochemical production  
578 of •OH.

579

## 580 **Conclusion**

581 This work aimed to investigate the effect of UVC irradiation on the ability of SRNOM to  
582 generate oxidant species, in particular •OH radicals under UVC. Through in-depth analytical  
583 and kinetic studies, we demonstrated that SRNOM irradiation drastically increased the pool of  
584 aliphatic carbonyls together with its capacity of photoinducing the degradation of glyphosate  
585 at 254 nm. Several experimental results suggest that •OH radicals contributed to this  
586 degradation. To better understand the role of carbonyls in the reaction, we studied the  
587 photodegradation of glyphosate in the presence of acetone and pyruvate. Experimental data  
588 were explained by a mechanism involving a chain reaction in which •OH radicals may be  
589 formed through the spontaneous decomposition of unstable hydroperoxides. The same  
590 mechanism might prevail in pre-irradiated SRNOM and explain its high efficiency to  
591 photodegrade glyphosate upon irradiation at 254 nm. These results show that in UVC  
592 treatments NOM could favour the degradation of micropollutants through its high capacity to  
593 generate very oxidant radicals. Such a pretreatment of NOM would deserve to be further  
594 studied in combination with other engineered water treatment systems.

595

596

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