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| 2 | photoxidant properties |
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Abstract : The present study aimed to investigate the changes in the chemical composition, 15 and in the optical and photooxidant properties of Suwannee River Natural Organic Matter 16 (SRNOM) induced by UVC (254 nm) treatment. The extent of the photodegradation was first 17 assessed by UV-visible/fluorescence spectroscopies and organic carbon analysis. An in-depth 18 investigation of the chemical changes was also conducted using liquid chromatography-mass 19 spectrometry and gas chromatography-mass spectrometry after derivatizations. A series of 20 mono, di and tricarbonyls and mono and dicarboxylic acids in C₁-C₆ were identified in 21 22 samples irradiated from 1 to 4 h. After 3 h of irradiation, carbonyls accounted for 46% of the organic carbon remaining in solution whereas carboxylic acids represented about 2%. Then, 23 we investigated the modifications of the photooxidant properties of SRNOM induced by these 24 chemical changes. At 254 nm, UVC pre-irradiated SRNOM photodegraded glyphosate 29 25 times faster than original SRNOM and the reaction was fully inhibited by 2-propanol (5×10^{-3}) 26 27 M). This enhanced photooxidant properties at 254 nm toward glyphosate was therefore reasonably due to •OH radicals formation, as confirmed by additional ESR measurements. A 28 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 study show that UVC pre-treatment of NOM can enhance the removal of water pollutants and 31 32 suggests a possible integration of a NOM pre-activation step in engineered water treatment sytems. 33

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

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40 Introduction

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

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

derivatization techniques with liquid chromatography-mass spectrometry (LC-MS) or gas chromatography-mass spectrometry (GC-MS). Formation of C₁-C₄ carbonyl compounds and C₂-C₅ carboxylic acids, amino acids and alcohols in UVC treatments was reported [Thomson et al, 2004; Agbaba et al, 2016; Zhong et al, 2017; Corin et al, 1996]. Some of these photoproducts were also found upon irradiation of NOM with natural or simulated solar-light ($\lambda > 290$ nm) [Brinkmann et al, 2003; de Bryun et al, 2011; Goldstone at al, 2002; Kieber et al, 1990].

The presence of NOM in UVC treatments has been generally reported to lower 72 73 treatment efficiency due to its ability to scavenge the reactive species generated under irradiation and/or to absorb photons competitively, therefore decreasing the degradation rate 74 of target compounds [Wang et al, 2016]. However, NOM is able to generate oxidant species 75 such as hydroxyl radicals (•OH), singlet oxygen $({}^{1}O_{2})$ and triplet excited states $({}^{3}NOM^{*})$ 76 under irradiation [Vione et al, 2014] and can also promote the degradation of contaminants 77 during UVC treatment [Lester et al, 2013]. The photosensitizing properties of NOM may 78 79 evolve during the UVC treatment because NOM itself undergoes chemical changes. Yet, to the best of our knowledge, very few studies investigated the effect of such modifications on 80 the ability of NOM to generate photooxidants in the course of engineered water treatments. 81 Treatments of NOM with hypochlorous acid and ozone were reported to increase its capacity 82 to generate ¹O₂ in simulated solar light due to the possible formation of quinone-like 83 molecules [Mostafa and Rosario-Ortiz, 2013; Leresche et al, 2019] but also to decrease its 84 capacity to generate ³NOM* due to photosensitizers destruction [Wenk et al, 2015]. On the 85 other hand, UV/chlorine treatment of NOM at high chlorine dosage was found to increase its 86 ability to generate ³NOM^{*}, ¹O₂, and •OH, upon irradiation within the range 290-400 nm 87 [Zhou et al, 2021]. Again, these effects were proposed to be due to the formation of quinone 88 and ketone functional groups. 89

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

104

105 Material and methods

106 Chemicals

SRNOM (2R101N) was purchased from the International Humic Substances Society (IHSS). 107 Glyphosate (99.7%) and H_2O_2 (> 30%) were obtained from Fluka. Methylglyoxal (40% in 108 109 weight), pyruvic acid (98%), glycolic acid (98%), acetone (> 99.5%), 2,4,6-trimethyphenol (TMP, certified reference material), furfuryl alcohol (FFA, analytical grade), terephtalic acid 110 (98%), hydroxyl-terephtalic acid (97%), 2,4-dinitrophenylhydrazine (DNPH, 97%), 111 bis(trimethylsilyl)trifluoro-acetamide containing 1% trimethylchlorosilane (BSTFA + 1% 112 TMCS, 98.5% exluding TMCS), NaH_2PO_4 (\geq 99.5%), Na_2HPO_4 (\geq 99%), horseradish 113 peroxidase (52 units per mg of solid), 4-hydroxyphenylacetic acid (98%), 5,5-dimethyl-1-114

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 M Ω cm and DOC < 0.1 mg L⁻¹. All these 118 chemicals were used as received.

119 UVC pre-irradiation of SRNOM

Briefly, 10 mg of SRNOM were dissolved in 250 ml of purified water to reach a 120 concentration of 40 mg L⁻¹. SRNOM solutions were buffered at pH 7 using phosphate buffers 121 (10^{-3} M) except for experiments conducted to monitor the pH evolution during irradiation or 122 123 designed to the detection of carboxylic and hydroxylic intermediates. In these cases, SRNOM solutions were neutralized to $pH = 7 \pm 0.2$ using freshly prepared NaOH (0.1 M). All the 124 solutions were stored at 4°C. SRNOM solutions (30 mL) were poured in a quartz glass 125 cylindrical vessel (2 cm i.d. \times 19 cm) and were irradiated in a device equipped with 4 126 germicidal tubes (253.7 nm, General Electric, 15 W). The photon flux entering the solution, 127 corresponding to 2.9×10^{-6} Einstein.L⁻¹.s⁻¹, was calculated by measuring the rate of 128 glyphosate loss in the presence of H₂O₂ (SI-Text 1, Fig SI-1). SRNOM solutions were 129 irradiated for 1 h, 2 h, 3 h and 4 h in separate experiments and labelled SRNOM_{1h}, SRNOM_{2h}, 130 SRNOM_{3h}, and SRNOM_{4h}, respectively. Irradiated solutions were used for analyses or 131 sensitizing investigations within the 24 h following irradiation. 132

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

5050 TOC analyser. Carbonyls contained in SRNOM and irradiated SRNOM were analyzed 140 by DNPH derivatization [Soman et al, 2008] (SI Text 2). Analyses were performed by ultra-141 high performance liquid chromatography (UHPLC) coupled to high resolution mass 142 143 spectrometry (HRMS). HRMS was performed on an Orbitrap Q-Exactive (Thermoscientific) coupled to Ultimate 3000 RSLC (Thermoscientific) UHPLC. Analyses were run in negative 144 (ESI⁻) electrospray modes. The column was a Kinetec EVO C₁₈ 100 mm / 2.1 mm, 1.7 µm 145 146 (Phenomenex). Details of separation conditions are given in (SI Text 3). Molecular formulas were obtained setting the difference between experimental and accurate masses to ≤ 5 ppm 147 148 while structures are proposed based on the number of DNPH molecules linked to carbonyls and on the number of double bonds in the carbonyl (NDB). In several cases, several isomers 149 are possible and given structures are thus only indicative. Pyruvic acid and methylglyoxal 150 were used as references to estimate the concentration of the other carbonyls (SI Text 3 and 151 Fig. SI-2). 152

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

SRNOM and SRNOM_{3h} were also analyzed by ionic Chromagraphy-Mass spectrometry (ICMS). Details are given in SI-text 5.

166

167 Sensitizing properties of original and UVC pre-irradiated SRNOM

Glyphosate was used to probe the formation of very oxidant species such as •OH from 168 original and pre-irradiated SRNOM solutions at 254 nm. The solutions containing glyphosate 169 (10^{-5} M) and SRNOM were prepared by adding 25 μ L of the stock solution of glyphosate (10^{-5} M) 170 2 M) to 10.2 mL of SRNOM (40 mg L⁻¹) and by adding purified water to reach the final 171 172 volume of 25 mL. For SRNOM_{3h} solutions, the same spike of glyphosate was added to 25 mL of non diluted solution. This way, the two solutions showed the same absorbance of 0.34 at 173 254 nm. Then, 15 mL of each solution were irradiated in the above-described device. 2-174 Propanol was used as a quencher of \cdot OH. Glyphosate (10⁻⁵ M) was also irradiated in the 175 presence of acetone (10⁻⁴ M), pyruvic acid (10⁻⁴ M), H₂O₂ (10⁻⁵ M), acetone (10⁻⁴ M) + H₂O₂ 176 (10^{-5} M) . Furthermore, acetone (10^{-4} M) was irradiated alone and in mixture with H₂O₂ (10^{-5} M) 177 and 10⁻³ M). All these experiments were conducted in air-saturated solutions. The effect of 178 oxygen on the rate of glyphosate photodegradation in the presence of SRNOM_{3h} was studied 179 by saturating the solution with N₂. Glyphosate concentration was monitored by UHPLC-180 by integrating peak area at m/z = 168.0056 (± 5 ppm). AMPA HRMS 181 (aminomethylphosphonic acid) with m/z = 110.0002 (± 5 ppm) was the only glyphosate 182 photoproduct detected. Acetone loss and photoproducts formation were monitored by 183 derivatization with DNPH followed by UHPLC-HRMS analysis. Photodegrading properties 184 of SRNOM and SRNOM_{3h} solutions were also investigated under irradiation between 300 and 185 400 nm. Both solutions were diluted by a half during preparation of mixtures. Terephthalic 186 acid (2 × 10⁻⁵ M) was used to probe •OH radicals, 2,4,6-trimethyphenol (2 × 10⁻⁵ M) to probe 187 ³SRNOM^{*} and ³SRNOM_{3h}^{*} and furfuryl alcohol (5.8 \times 10⁻⁵ M) to trap ¹O₂. Solutions 188

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

193

194 Peroxides titration

Peroxides concentration was measured by the spectrofluorimetric quantification method
previously described by Miller and Kester, 1988. Details of the exeriments are given in SItext 6.

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ESR experiments

ESR experiments were carried out using a Bruker EMX, 9.8 GHz equipped with a cavity ER4105DR and a xenon lamp (Xenovia 200 - 900 nm). The ESR spectra were obtained at room temperature under irradiation inside the cell of the following mixtures : DMPO (25 mM) in the presence of SRNOM (20 mg L⁻¹), SRNOM_{3h} or H₂O₂ (5 × 10⁻³ or 10⁻⁵ M).

204

205 Results and discussion

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

Fig. 1A shows that the SRNOM solution progressively photobleached. The absorbance at 254 nm declined by 59% and 77% after 3 and 4 h of irradiation, respectively (Table 1). The reduction of DOC as a function of irradiation time revealed that SRNOM also underwent substantial mineralization (35% after 4 h) while the specific ultraviolet absorbance (SUVA) decreased by 42% and 64% after 3 and 4 h of irradiation, respectively, indicating a loss of 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.

Irradiation also led to a breakdown of fluorescent species in accordance with previous 215 studies [Patel-Sorrentino et al, 2004]. The fluorescence intensity at the emission maximum 216 declined by 53% after 3 h of irradiation, and by 68% after 4 h (Fig 1 C). Fig 1D also shows 217 that the blue part of the fluorescence emission spectra disappeared the fastest leading to 218 emission spectra red-shifted by 10 - 15 nm or to a band contraction. On the contrary, 219 220 treatment of NOM with radicals such as SO₄• [Zhang et al, 2019] or •OH [Varanasi et al, 2018] was reported to induce a blue-shift of fluorescence emission spectra attributed to 221 preferential degradation of high molecular weight moieties into smaller entities. In these 222 treatments, radicals are expected to react preferentially with biggest macromolecules offering 223 the largest number of attack sites while in photolytic treatment the reactivity of generated 224 225 excited states is the critical factor. Our results suggest that smaller fluorescent entities initially present in SRNOM or produced in the course of the treatment were more subject to 226 227 photodegradation than larger ones. The reasons could be that they were more light absorbing because more oxidized and/or underwent less desactivation processes than bigger constituents 228 being less embedded in large structures than these latter. 229

230

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

Table 2 summarizes the chemicals detected by DNPH or BSTFA derivatization and by CI/MS in SRNOM before irradiation and after irradiation. Detailed MS data are given in Figure SI-3, Tables SI-1 to SI-3 and the structures of photoproducts observed in irradiated samples are shown in Figure 2. In starting SRNOM, we detected 5 carbohydrates in C_5 and C_6 (xylose, rhamnose, fucose, glucose and galactose) mentionned in the IHSS web page, along with 2 monocarboxylated alkanes in C_3 and C_{18} (glyceric and oleic acids) and 3 dicarboxylated alkanes in C₆, C₉ and C₁₂ (hexanedioic, nonanedioic and dodecanedioic acids)
(Tables 2 and SI-1). Several carbonyls were found, but only as traces.

In SRNOM_{3h}, none of the carbohydrates observed in SRNOM were found while 11 240 carboxylated alkanes were detected: 5 monocarboxylated in C_1 (formic acid), C_2 (acetic and 241 glycolic acid), C₃ (lactic acid) and C₄ (4-aminobutanoic acid), 7 dicarboxylated alkanes in C₂ 242 (oxalic acid), C₃ (malonic, tartronic, dihydroxymalonic acids), C₄ (butanedioic and malic 243 244 acids), C₅ (glutaric acid) and C₆ (tricarballylic acid) (Tables 3 and SI-2). In all the irradiated samples, 16 carbonyls in C_1 - C_5 were detected among them 7 monocarbonyls (formaldehyde, 245 acetaldehyde, glycoladehyde, glyoxylic acid), 7 dicarbonyls (glyoxal, methylglyoxal, 246 butenedial) and 2 tricarbonyls. Some of these compounds were already reported to be 247 produced by irradiation of natural surface waters or synthetic waters containing NOM with 248 natural or simulated solar-light, by ozone treatment or by UV-based AOPs of solutions of 249 250 humic substances. This is the case for formic, acetic and oxalic acids [Brinkmann et al, 2003; Goldstone et al, 2002], formaldehyde, acetaldehyde, glyoxal and methylglyoxal [Thomson et 251 al, 2004; Agbaba et al, 2016; Zhong et al, 2017; de Bryun et al, 2011; Kieber et al, 1990], 252 malonic and butanedioic acids [Corin et al, 1996], and pyruvic acid [Thomson et al, 2004]. 253

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

The total pool of C_1 - C_5 carbonyls was estimated by summing the individual 262 concentrations. Figure 3B shows that their cumulative concentration increased during the first 263 2 h of irradiation to reach the value of 2.8×10^{-4} M. Based on these concentrations and on the 264 DOC measurements, the mass percentage of carbon atoms contained in the detected carbonyls 265 could be calculated using Eq 1. This percentage was maximum after 3 h of irradiation where it 266 reached 46% (Figure 3B). This high value demonstrates the very important contribution of 267 C₁-C₅ carbonyls to the pool of photoproducts. As most of these compounds poorly absorbed 268 below 300 nm, their high concentration explains the unchanged spectrum shape following 269 irradiation. 270

271

$$Mass \ percentage_t = \frac{\sum_{i=1}^{i=n} [c_i]_t \times M_i}{DOC_t}$$
 Eq 1

where $[c_i]_t$ and M_i are the concentration at time t and the molecular mass of carbonyl i, and DOC_t is the organic carbon content in the solution at time t.

The concentration of carboxylic acids detected in SRNOM_{3h} are shown in Table SI-5. 275 In general, BSTFA-GC-MS and CI-MS analyses gave consistent results regarding the 276 concentration estimations. BSTFA-GC-MS was however less performant than CI-MS in the 277 analysis of compounds containing 2 or 3 CO₂H or OH functions such as tartronic, 278 dihydroxymalonic acid, oxalic acid and tricarballylic acids. The difficulty to solubilize 279 lyophilized SRNOM_{3h} in acetonitrile to conduct the BSTFA derivatization or a partial 280 derivatization of these compounds probably explain these discrepancies. Malic, oxalic, 281 butanedioic, glycolic, and malonic acids were the most concentrated acids. However, their 282 concentration in SRNOM_{3h} that laid below 2.8×10^{-6} M, were much lower than those of 283 carbonyls. Eq 1 allowed to determine that the detected carboxylic acids contained only 2% in 284 285 mass of the SRNOM_{3H} carbon atoms.

287

Nitrate ions were also detected by CI-MS in SRNOM at a level of 2.9×10^{-6} M, but not in SRNOM_{3b}.

The detection of all these compounds suggests that the photodegradation of SRNOM 288 under UVC resulted from a complex set of reactions involving the direct photolysis of 289 SRNOM constituents as well as their oxidation by the radicals generated in the course of the 290 irradiation. Many radicals such as R•, RO•, RO₂•, HO₂•/O₂•⁻ and •OH can be formed by C-C, 291 C-O, and O-O bond cleavage, phenyl-O and RCO₂ photoionization, addition of oxygen on 292 293 radicals and various radicalar attacks. Once formed, these radicals could contribute to further degradation of SRNOM constituents and of their by-products. Among them, •OH radical is 294 295 likely to play a significant role for several reasons. It is the most oxidant species able to react with a wide variety of chemicals by addition on double bonds or by H atom abstraction 296 [Buxton et al, 1988]. NOM was shown to generate •OH radicals [Vaughan and Blough, 1998; 297 298 Page et al, 2011; McKay et al, 2015; Gan et al, 2008; Sun et al, 2015; Dong et al, 2012; Aguer and Richard, 1999] under irradiation. In reactions where •OH radicals are purposely 299 300 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 proposed to occur via the intermediary formation of •OH radicals [Tafer et al, 2016], yielded 302 303 glycolic, lactic, and butanedioic acids, acetaldehyde, glycoaldehyde, methylglyoxal, $C_4H_4O_3$, and $C_3O_3H_2$ that were also detected in the present work. 304

305

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

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

SRNOM and SRNOM_{3h} were tested at the same absorbance at 254 nm (0.34). In the presence 311 of SRNOM, glyphosate (10⁻⁵ M) disappeared with a rate constant k of 0.0013 \pm 0.0002 min⁻¹ 312 in air-saturated solution (Figure 4A and Table 3). Making the hypothesis that the reaction was 313 314 due to the reaction of glyphosate with •OH radicals, we used this rate constant to estimate the quantum yield of •OH radicals formation by SRNOM (Φ_{OH}^{SRNOM}) in the first stages of the 315 reaction. Once formed by process 1, •OH radicals react with glyphosate ($k_{gly} = (3.37 \pm 0.10) \times$ 316 10⁷ M⁻¹ s⁻¹, Vidal et al, 2015) (process 2) and with SRNOM (process 3). We took for k_{SRNOM} 317 the value of $1.6 \times 10^8 M_{\rm C}^{-1} {\rm s}^{-1}$ reported in the literature for Suwannee river fulvic acid 318 319 [Westoffer et al, 2007].

320

| 321 | $SRNOM + h\nu \rightarrow SRNOM^* \rightarrow \bullet OH$ | I_a, Φ_{OH}^{SRNOM} | (1) |
|-----|---|--------------------------|-----|
| 322 | •OH + Glyphosate \rightarrow | k_{Gly} | (2) |
| 323 | •OH + SRNOM \rightarrow | k _{srnom} | (3) |

324

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

326

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

327

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

In the presence of SRNOM_{3h} and in air-saturated solution, glyphosate disappeared 333 much faster than in the presence of SRNOM (Figure 4A) with $k = 0.038 \pm 0.004 \text{ min}^{-1}$ (Table 334 3). In N₂-purged SRNOM_{3h} solution, the glyphosate photodegradation rate was significantly 335 reduced compared to the one conducted in air-saturated medium (k = 0.002 ± 0.002 min⁻¹ in 336 the first 10 min of the reaction, Figure 4A, Table 3) demonstrating the important role played 337 by oxygen in the reaction. Moreover, we irradiated glyphosate and SRNOM_{3h} in the presence 338 of 2-propanol to determine whether •OH radicals were involved in the loss of glyphosate. 339 Using $k_{2-propanol} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [Buxton et al, 1998] for the bimolecular rate constant of 340 reaction between •OH and 2-propanol : 341

342

•OH + 2-propanol \rightarrow k_{2-propanol}

343 we added 5×10^{-3} M of 2-propanol expecting an inhibition of the reaction > 90% based on 344 k_{SRNOM3h}[SRNOM_{3h}] ~ 9×10^4 s⁻¹, as for SRNOM. The inhibition was of 90% (Figure 4A, 345 Table 3) in accordance with a significant contribution of •OH.

(4)

Spin trap experiments using DMPO as the spin-trapping reagent were also conducted to confirm the formation of •OH radicals. Figure 5 shows that the four-line signal with an intensity ratio 1:2:2:1 characteristic of the DMPO-OH• adduct was not detected when DMPO was irradiated in the presence of SRNOM (plot a) or H_2O_2 (10⁻⁵) (plot c) while it was observed with SRNOM_{3h} (plot b) and H_2O_2 (5 × 10⁻³ M) (plot d). Again, this result is in line with the production of •OH radicals upon irradiation of SRNOM_{3h} in UVC.

Postulating that the disappearance of glyphosate was only due to the reaction with •OH, we made the same calculation for SRNOM_{3h} as for SRNOM, after having replaced processes 1 and 2 by processes 1' and 3' respectively:

355

| 356 | $SRNOM_{3H} + h\nu \rightarrow$ | $SRNOM_{3H}^* \rightarrow$ | •OH | $I_a, \Phi_{OH}^{SRNOM3h}$ | (1') |
|-----|---------------------------------|----------------------------|-----|----------------------------|------|
| 357 | •OH + SRNOM _{3H} $-$ | → | | k _{SRNOM3h} | (3') |

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

373

4. Peroxides formation and role of H₂O₂ in the oxidant properties at 254 nm

375 Peroxides are sources of •OH radicals through direct photolysis (process 5) or photo-Fenton reaction and we quantified their formation in our system. Measurements of H₂O₂ and 376 $RO_2H + RO_2R$ were performed on SRNOM and SRNOM_{3h} irradiated for 30 min (Figure 5). 377 In SRNOM, H_2O_2 and $RO_2H + RO_2R$ accumulated linearly. After 30 min of irradiation, the 378 total concentration of $H_2O_2 + RO_2H + RO_2R$ was equal to 16 μ M; H_2O_2 was by far the most 379 abundant species (14.2 μ M) while RO₂H + RO₂R contributed to the pool of peroxides in a 380 minor way (1.8 µM). In SRNOM_{3h}, the peroxides formation was auto-inhibited, slowing 381 down after 10 min. The total concentration reached 15.8 μ M after 30 min ; H₂O₂ and RO₂H + 382

RO₂R were in equivalent amounts of ~ 8.0 μ M. The formation of H₂O₂ in the photolysis of NOM is well documented in the literature [Garg et al., 2011]. It is formed by dimutation of O₂⁻⁻ that arises from reduction of dissolved O₂. Peroxides and hydroperoxides are generated after the reaction of R⁻ radicals with dissolved O₂ to yield RO₂⁻ and the reaction of these peroxyl radicals with O₂⁻⁻/HO₂⁻ [Sun et al., 2021].

To determine the contribution of H_2O_2 to the formation of •OH via process (5), we proceeded as follows. We first measured R_{Gly} in the presence of H_2O_2 (10⁻⁵ M) alone. The value of 1.5×10^{-9} M⁻¹ s⁻¹ allowed us to check that glyphosate reacted with •OH and to measure the photon flux I₀ in the irradiation device (SI-Text 1). Then, we calculated R_{Gly}^{H2O2} in SRNOM solution using Eq 2, supposing that the photolysis of H_2O_2 produced during the irradiation of SRNOM was the only source of •OH through process 5 (SI-Text 5).

394
$$H_2O_2 \rightarrow \bullet OH \qquad \emptyset_{OH}^{H2O2}$$
 (5)

395

$$R_{Gly}^{H2O2} = I_{a,H2O2}^{SRNOM} \, \phi_{OH}^{H2O2} \frac{k_{gly} \, [Gly]}{k_{gly} [Gly] + k_{SRNOM} \, [SRNOM] + k_{H2O2} \, [H2O2]} \quad EQ2$$

396

Taking $[H_2O_2] = 14 \ \mu M$ (corresponding to the highest value reached for SRNOM), $\varepsilon_{H2O2} =$ 397 19.6 M⁻¹ cm⁻¹ at 254 nm, A₂₅₄ =0.34 for SRNOM and $\ell = 2$, we calculated $I_{a,H202}^{SRNOM}$ using the 398 Beer-Lamber law for a mixture (SI-Text 8). Then, taking $k_{H2O2} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [Stephan et 399 al, 1996], we got that glyphosate trapped 0.38% of •OH and using $\Phi_{OH}^{H2O2} = 1$ [Yu and 400 Barker, 2003], we finally obtained $R_{Glv}^{H2O2} = 7.0 \times 10^{-12} \text{ M s}^{-1}$. In the case of SRNOM_{3h}, we 401 took $[H_2O_2] = 8 \ \mu M$ and the same calculation led to $R_{Gly}^{H2O2} = (3.0-9.0) \times 10^{-12} \ M \ s^{-1}$. Both 402 values are very small compared to the experimental values 2.2×10^{-10} M s⁻¹ and 6.5×10^{-9} M 403 $s^{\text{-1}}$ respectively measured for SRNOM and SRNOM_{3h} and it can be concluded that the 404 photochemical decomposition of titrated hydroperoxides negligibly contributed to the 405

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

409

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

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

425

•OH + pyruvate products (6) $k_{pyruvate}$ \rightarrow

426

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

for intermediary carbonyls, acetone increased the rate of glyphosate photodegradation and the 431 reaction was also auto-accelerated (Figure 6A, Table 3). During the first 10 min of reaction, 432 an averaged $k = 0.002 \pm 0.001 \text{ min}^{-1}$ was obtained while, between 10 and 30 min, we 433 measured k = 0.024 ± 0.003 min⁻¹. In parallel, the decay of acetone was monitored by 434 UHPLC-HRMS after DNPH derivatization. Acetone also disapppeared by an autoaccelerated 435 reaction (Figure 6B). Between 0 and 10 min, the loss of acetone was lower than 5% 436 corresponding to a rate of acetone photodegradation ($R_{acetone}$) < 0.9 × 10⁻⁸ M s⁻¹ while, 437 between 10 and 40 min, acetone disappeared by 43% and $R_{acetone}$ was equal to 2.4×10^{-8} M s⁻¹ 438 (Table 3). During this reaction H₂O₂ was formed (Figure 6B). The H₂O₂ production was of 2 439 µM between 0 and 10 min and 10 µM between 10 and 30 min which mirrored the 440 autoaccelerated decrease of glyphosate and acetone. In the presence of 2-propanol (10^{-4} M) 441 and acetone (10⁻⁴ M), glyphosate disappeared by 10% instead of 42% in the absence of 2-442 propanol after 30 min of irradiation (Figure 6A, Table 3) confirming again a significant 443 contribution of •OH in the reaction (75%). 444

Acetone was also irradiated alone to check that the observed auto-acceleration was not 445 due to the presence of glyphosate. At 2.4×10^{-4} M, acetone also disappeared in an auto-446 accelerated reaction with $R_{acetone} < 0.9 \times 10^{-8} \text{ M}^{-1} \text{ s}^{-1}$ between 0-10 min and $R_{acetone} = 3.9 \times 10^{-8}$ 447 M⁻ s⁻¹ between 10-30 min (Table 3). The photoproducts were pyruvic acid, methyl glyoxal, 448 hydroxyacetone, formadehyde as described by Stephan and Bolton (1999) when they studied 449 the photolysis of acetone in the presence of H₂O₂ at 254 nm. Using the quantum yield of 450 acetone photodegradation in diluted solutions (0.061), and $\varepsilon_{acetone} = 16 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm, it 451 is possible to calculate the rate of acetone photodegradation by direct photolysis 452 $R_{acetone}^{dp}$ using EQ3: 453

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

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

An autoaccelerated reaction is generally due to the accumulation of key intermediates. 460 Here, the intermediary chemicals were the acetone photoproducts and peroxides, among 461 which, H_2O_2 . We therefore studied the effect of H_2O_2 , used a hydroperoxide model, at the 462 concentration of 10^{-5} and 10^{-3} M on the photodegradation of acetone (2.4 \times 10⁻⁴ M). The 463 photodegradation of acetone was fast till the very beginning of the irradiation ($R_{acetone} = 3.5 \times$ 464 10^{-8} and 1.8×10^{-7} M s⁻¹, respectively, Table 3) and no auto-accelerating effect was observed. 465 In this mixture, acetone can disappear by reaction with \cdot OH produced from H₂O₂ photolysis 466 (process 7, $k_{acetone} = 1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, Buxton et al, 1998). Process 8 is a potential competiting 467 pathway of •OH disappearance ($k_{H2O2} = 2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ Buxton et al, 1998). 468

469

| 470 | •OH + acetone | \rightarrow | products | (7) $k_{acetone}$ |
|-----|---------------------------------------|---------------|----------|-----------------------|
| 471 | •OH $+$ H ₂ O ₂ | \rightarrow | products | (8) k _{H2O2} |

472

For $[H_2O_2] = 10^{-3}$ M and [acetone] = 2.4×10^{-4} M, process 8 was expected to significantly reduce the percentage of •OH radicals trapped by acetone. Taking into account that acetone should trap about 50% of •OH, one obtains $R_{acetone} = 1.3 \times 10^{-7}$ M.s⁻¹ against 1.8×10^{-7} M s⁻¹ measured experimentally. For $[H_2O_2] = 10^{-5}$ M and [acetone] = 2.4×10^{-4} M, process 8 was negligible, and acetone was expected to trap all the •OH radicals produced by H_2O_2 photolysis. Its rate of decay through process 7 ($R^{OH}_{acetone}$) was equal to 2.6×10^{-9} M s⁻¹ according to EQ 4.:

$$R_{acetone}^{OH} = I_0 \left(1 - 10^{-A_{H2O2}} \right) \phi_{OH}^{H2O2} \qquad EQ4$$

This calculated rate accounted for only 6.6% of the measured rate indicating that an additional radical source was responsible for acetone degradation. Then, we simultaneously irradiated glyphosate (10^{-5} M), H₂O₂ (10^{-5} M) and acetone (10^{-4} M). In this case, the glyphosate photodegradation was fast till the beginning of the irradiation (k = 0.016 min⁻¹) (Figure 6A, Table 3) showing that H₂O₂ or other hydroperoxides are important intermediaries in the reaction.

The results obtained for acetone can be tentatively explained by the chain-reaction 487 mechanism shown in Scheme 1. In the classical chain oxidation of a chemical RH bearing a 488 labile H atom, the initiator produces the primary radicals (process 9) that start the chain 489 through a transfer reaction by generating the radical R• (process 7). Then R• produces RO₂• 490 by adding O₂ (process 10) and RO₂• regenerates R• along to RO₂H by abstracting of a H from 491 RH (process 11). The longer the chain length, the faster the reaction; in fact, when the chain is 492 long enough, the rate of the propagation reactions becomes much higher than the rates of 493 initiation and of transfer. In our case, the calculated rate of acetone photolysis $R_{acetone}^{dp}$ 494 (process 9) was much lower than the experimental rate of acetone photodegradation 495 496 consistently with the involvement of a chain reaction.

The irradiation of acetone was expected to yield radicals by α -cleavage of the triplet excited state (process 9) [Pearson, 1963]. The triplet could also abstract a H-atom from methyl groups of acetone, however, neither acetone itself nor glyphosate were concentrated enough to compete significantly with the cleavage [Anpo and Kubokawa, 1977]. Due to the oxidation of these radicals and to the photolysis of the formed hydroperoxides, there should be a pool of initiating radicals in the system. The acetonyl radical, R•, formed by process 7 [Stephan et al, 1996] should easily react with oxygen (process 10) to yield the peroxyl radical ROO• [Stephan et al, 1996]. This peroxyl radical likely abstracted an H-atom from acetone (process 11) to regenerate the acetonyl radical and produce the hydroperoxide ROOH. The 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 formed in the complex mixture. However, while the reaction with •OH was evidenced, the 508 509 oxidation with the other radicals remains to be demonstrated. If we make the hypothesis that •OH contributed significantly to the glyphosate degradation, the source of •OH needs to be 510 explained. Indeed, calculations showed that the photolysis of the different hydroperoxides did 511 not yield enough radicals to explain the high rate of glyphosate degradation. An alternative 512 513 formation of •OH could be the spontaneous decomposition at room temperature of unstable hydroperoxides, here CH₃-CO-CH₂OOH (process 13). According to the works of Badiali et al 514 (2015) and Krapf et al (2016), the formation of very unstable hydroperoxides is plausible. 515 516 Therefore, despite processes 7, 10 and 11 still taking place, the key process became process 13 since it introduced a continuous source of •OH and RO• radicals. Consequently, the rate of 517 glyphosate degradation increased during the accumulation phase of ROOH, reaching the 518 519 maximal value rate when the RO₂H formation equaled the RO₂H decomposition.

520 CH_3 -CO-CH₂OOH \rightarrow CH₃-CO-CH₂O• + •OH

In the case of SRNOM_{3h}, carbonyls were present at 2.4×10^{-4} M and hydroperoxides 521 were potentially generated at a fast rate, therefore making it possible the mechanism already 522 proposed in the case of acetone to occur. In accordance, ROOH + ROOR were formed along 523 with H₂O₂. In SRNOM_{3h} solution, R_{glv} was equal to 6.3 \times 10⁻⁹ M s⁻¹. Considering that 524 glyphosate trapped between 0.3 and 0.8 % of •OH radicals in competition with SRNOM_{3H} 525 constituents, the rate of •OH formation should be comprised between $\sim 8 \times 10^{-7}$ and 2×10^{-6} 526 M s⁻¹. In the model solution containing glyphosate (10^{-5} M), H₂O₂ (10^{-5} M) and acetone (10^{-4} 527 M), Rgly was equal to 2.7×10^{-9} M s⁻¹. Considering that •OH contributed to the reaction at 528

(13)

75% and that glyphosate trapped 3% of •OH in competition with acetone, then the rate of •OH 529 formation should be equal to ~ 7×10^{-8} M s⁻¹. For acetone (2.4×10⁻⁴ M), it might be ~ 1.7 × 530 10^{-7} M s⁻¹. This value is smaller than that estimated for the SRNOM_{3h} solution, and several 531 explanations of this difference can be proposed: (i) SRNOM_{3h} was a much more complex 532 system than H_2O_2 + acetone and quantitative results cannot be directly transferable; 533 534 furthermore, calculation lays on an hypothetical value of the bimolecular reaction rate 535 constant of SRNOM_{3h} with •OH; (ii) Acetone was chosen as a model compound but among 536 the carbonyls formed in SRNOM_{3h}, some may absorb more than acetone, especially those 537 bearing double bonds, and/or photodissociate much more easily [Anpo and Kubokawa, 1977]; (iii) SRNOM $_{3h}$ also contained chemicals acting probably as better H-donors than acetone and 538 glyphosate, which should favour process 11 and thus the formation of unstable 539 hydroperoxides; (iv) Oxidant species other than •OH might contribute to the photodegradation 540 of glyphosate. 541

In the case of SRNOM, R_{Gly} was much higher than R_{Gly}^{H2O2} as for SRNOM_{3h} 542 suggesting that chain reactions might take place as for SRNOM_{3H}, although leading to a much 543 slower production of •OH. Accordingly, the 6-times less formation of ROOR+ROOH from 544 SRNOM than from SRNOM_{3h} suggests that unstable hydroperoxides should be produced in 545 smaller amounts by SRNOM than by SRNOM_{3h}. Spectral measurements showed that 546 SRNOM is much more aromatic than SRNOM_{3h} which constitutes an important difference in 547 terms of •OH reactions. The •OH radicals are known to add on phenols [Lundquist and 548 Eriksson, 2000] to finally produce unreactive phenoxyl radicals while they generate radicals 549 550 oxidable into hydroperoxides when they abstract hydrogen atoms from aliphatic compounds. Hence, the presence of carbonyls in SRNOM_{3h} could not only favour the formation of radicals 551 through their photolysis but also constitutes a pool of aliphatic compounds oxidable into 552 hydroperoxides. 553

AMPA was the main glyphosate photoproduct detected by UHPLC-HRMS (Figure 4B). In the literature, other oxidation products were also detected such as sarcosine [Chen et al, 2007], not detected in this work. After 30 min of irradiation, the highest yield of AMPA was measured with H_2O_2 (66%), followed by SRNOM_{3h} (62%), acetone (57%) and pyruvic acid (38%). Interestingly, when 2-propanol was added to acetone and pyruvate solutions, the yield of AMPA dropped to 10% and 17%, respectively. The formation of AMPA may be thus an indirect evidence of the involvement of •OH radicals in the photodegradation.

561

562 5. Effect of SRNOM pre-irradiation on •OH, ¹O₂ and ³SRNOM* formation under

563 simulated solar light

We also compared the ability of SRNOM and SRNOM_{3h} to photoproduce 564 photooxidants ³SRNOM^{*}, ¹O₂ and •OH in simulated solar-light. After the normalization for 565 566 light absorption, the rate of 2,4,6-trimethyphenol was found to be 1.5 times higher in SRNOM than in SRNOM_{3H}, in accordance with lower rate of ³SRNOM* formation. Therefore, 567 chromophores yielding ³SRNOM* were partly degraded under UVC irradiation. In the case of 568 569 $^{1}O_{2}$ titrated using furfuryl alcohol, we found rates of formation varying by less than 10% between SRNOM and SRNOM_{3h}. At last, results on terephthalic acid used to estimate the rate 570 of •OH formation showed a higher rate of •OH formation in SRNOM_{3h} solution than in 571 SRNOM solution. Taking $k_{SRNOM} = 1.6 \times 10^8 M_{C}^{-1} s^{-1}$ and $k_{SRNOM3h} = 0.7 \times 10^8 M_{C}^{-1} s^{-1}$ for the 572 bimolecular rate constants of reaction with •OH, we got a rate of •OH formation higher by 573 40% for SRNOM_{3h} solution than for SRNOM solution. This enhancement was much lower 574 than the one observed at 254 nm with glyphosate. The dependence of the •OH formation 575 enhancement on the irradiation wavelength supports the hypothesis of the involvement of 576 577 poorly conjugated and light absorbing carbonyl compounds in the photochemical production of •OH. 578

580 Conclusion

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

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