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New route to toxic nitro and nitroso products upon irradiation of micropollutants mixtures containing imidacloprid: role of NO_x and effect of natural organic matter

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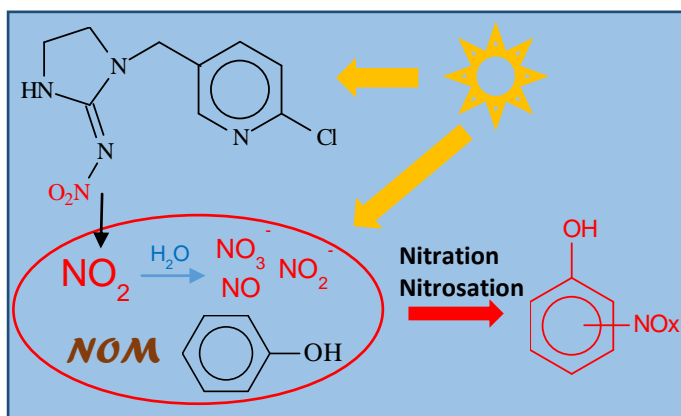
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6 **ABSTRACT**

7 In this study we reveal the capacity of imidacloprid (a neonicotinoid insecticide) to
8 photoinduce nitration and nitrosation of three aromatic probes (phenol, resorcinol, tryptophan)
9 in water. Using a gas-flow reactor and NO_x analyzer, the production of gaseous NO/NO₂ was
10 demonstrated during irradiation (300-450 nm) of imidacloprid (10⁻⁴ M). Quantum calculations
11 showed that formation of NO_x proceeds via homolytic cleavage of the RN-NO₂ bond in the
12 triplet state. In addition to gaseous NO/NO₂, nitrite and nitrate were also detected in water,
13 with the following mass balance: 40±8% for NO₂, 2±0.5% for NO, 52±5% for NO₃⁻ and
14 16±2% for NO₂⁻. The formation of nitro/nitroso probe derivatives was evidenced by high
15 resolution mass spectrometry and their yields were found be ranging between 0.08% and
16 5.1%. The contribution of NO₃⁻/NO₂⁻ to the nitration and nitrosation processes was found
17 minor under our experimental conditions. In contrast, the addition of natural organic matter
18 (NOM) enhanced significantly the yields of nitro/nitroso derivatives, likely via production of

19 triplet excited states ($^3\text{NOM}^*$) and $\text{HO}\cdot$. These findings reveal the importance of investigating
20 the photochemical reactivity of water contaminants in mixture to better understand the
21 cocktail effects on their fate and toxicity.

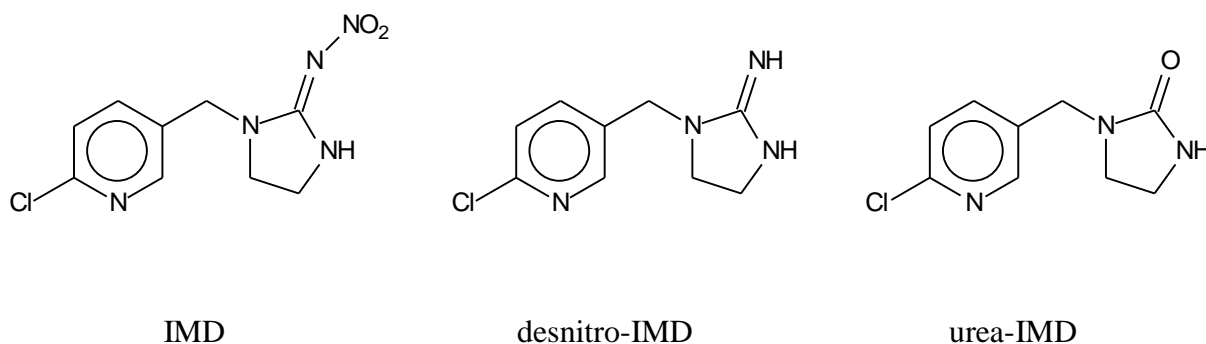
22 Graphical abstract



23 **INTRODUCTION**

24 Imidacloprid (1-[(6-chloropyridin-3-yl)methyl]-N-nitro-imidazolidin-2-imine, IMD, Scheme
25 1) is a widely used and effective neonicotinoid insecticide.¹ IMD, like other neonicotinoids, is
26 used in a variety of crops and its applications have been recently extended to domestic sector
27 and animal health.¹ Once released in the environment, it can reach the aquatic, atmospheric
28 and terrestrial compartments and be in contact with a lot of living organisms.²⁻⁴ IMD affects
29 the central nervous system of insects⁵ and there are increasing concerns about its deleterious
30 effects with confirmed toxicity for pollinators, especially bees.⁶ Toxicity or adverse effects in
31 other species has been also reported⁷⁻⁹.

32



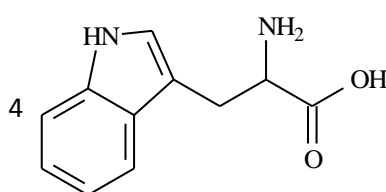
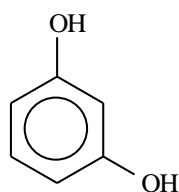
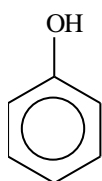
Scheme 1: Molecular structure of IMD and its main photoproducts

33 Several studies have been performed to investigate the fate of IMD under solar light, mainly
34 in aqueous solutions^{1, 10-13} on plant leaves and cuticles¹⁴⁻¹⁶ and more recently on solid thin
35 films¹⁷. Desnitro -IMD (1-[(6-chloropyridin-3-yl)methyl]imidazolidin-2-imine) was reported
36 to be the main photoproduct and the urea-IMD (1-[(6-chloropyridin-3-
37 yl)methyl]imidazolidin-2-one), a minor photoproduct (Scheme 1).¹⁶ The formation of these
38 by-products seems to imply the cleavage of the N-NO₂ bond; however, the fate of NO₂ is not
39 yet clear. Recently, the formation of gaseous nitrogen oxides during the irradiation of IMD at
40 the surface of a germanium attenuated total reflectance (ATR) crystal was investigated.¹⁷ The

41 authors detected nitrous oxide (N₂O) which was proposed to be formed by recombination of
42 detached NO₂ with the IMD fragments in the electronic ground state.

43 In previous studies, we showed that the fungicides chlorothalonil and thiophanate-methyl can
44 photoinduce the degradation of other pesticides during irradiation.^{18,19} These reactions can
45 take place in surface waters where fungicides are present together with a wide range of other
46 chemicals and on solid supports such as the surface of leaves where pesticides are often
47 applied in combination. However, the effect that a pollutant can have on another pollutant
48 remains largely overlooked in photochemical studies and little is known on the transformation
49 of photostable pollutants *via* light induced reactive intermediates of other co-pollutants. The
50 ability of IMD to release NO₂ upon irradiation makes this compound important to study in
51 this context since nitration of chemicals have been reported in a lot of systems generating NO₂
52 ²⁰⁻²⁸.

53 The goal of this study was thus to explore the formation of reactive NO_x *via* IMD photolysis
54 and their reactivity towards surrogates of water contaminants and typical moieties of natural
55 organic matter (phenol, resorcinol and tryptophan). In particular, we investigated the
56 formation of nitro and nitroso-derivatives, two potentially toxic categories of compounds,
57 from the three selected probes under polychromatic irradiation (300-450 nm) in the presence
58 of IMD. Experiments were carried out using a flow-tube reactor equipped with NO_x analyzer
59 whereas the formation of by-products was characterized using high resolution UHPLC-ESI-
60 MS. Theoretical calculations were also performed to elucidate the mechanisms of NO_x
61 formation. To the best of our knowledge, this is the first study reporting on the measurement
62 of NO_x during irradiation of IMD in water and on their role in nitrosation/nitration of other
63 water pollutants. Environmental implications of this light-induced indirect degradation are
64 discussed.



phenol

resorcinol

tryptophan

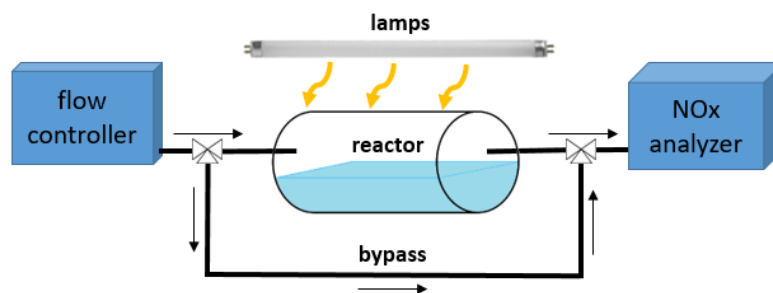
65 **Scheme 2:** Selected probes

66 **MATERIALS AND METHODS**

67 **Chemicals and materials.** Imidacloprid (Pestanal[®], analytical standard), resorcinol (purity
68 99%), phenol (purity $\geq 99.5\%$), L-tryptophan (purity $\geq 98\%$) and 2,4-dinitrophenylhydrazine
69 (DNPH, purity 97%) were purchased from Sigma-Aldrich and used as received. Sodium
70 nitrite (Rectapur 98%), sodium nitrate (Fluka, purity 99%), 2 and 4-nitrophenol (Fluka, purity
71 $\geq 99\%$) and 4-nitrosophenol (Aldrich-Chemie, purity 60% due to a content of water of 40%)
72 were also used without further purification. Suwannee River NOM (2R101N) was purchased
73 from IHSS. Water was purified using a reverse osmosis RIOS 5 and Synergy (Millipore)
74 device (resistivity 18 M Ω cm, DOC < 0.1 mg.L⁻¹). All solvents or other reactants were of the
75 highest grade available.

76 **Irradiations.** Two different irradiation devices were used. To monitor NO_x formation in the
77 gas phase, device 1, was designed with a cylindrical Pyrex gas flow-reactor (0.65 L, length 27
78 cm and diameter 5.7 cm) containing 200 mL of IMD solution (10⁻⁴ M or 25.6 mg.L⁻¹) and
79 irradiated from the top with two fluorescent tubes (Sylvania F15W/BL 368, 438 mm \times 26 mm,
80 300-450 nm, λ_{max} at 365 nm, see Figure SI-1) placed at a distance of 5 cm. The rate of
81 incident light entering the solution was measured using a QE65000 (Ocean optics) radiometer, it
82 was equal to 1.3 $\times 10^{16}$ Photon.cm⁻².s⁻¹. The gas flow-reactor was connected to a NO_x
83 chemiluminescence analyzer (Thermo Scientific i-42 NO_x analyzer) as shown in Figure 1.
84 Experiments were carried out under continuous flow of clean air, to reduce the residence time
85 of NO_x and minimize NO₂ photolysis. Gaseous inlet of the reactor was connected to flow

86 controllers for N₂ and O₂ (model Brooks 4800 series) allowing to select the atmosphere under
87 which the irradiations were performed (pure N₂, pure O₂ or a 80/20 O₂/N₂ mixture) and to
88 adjust the flow rate to 0.7 L min⁻¹. Background levels of NO_x in the gas inlet were negligible
89 (<0.4 ppbv). Before irradiation, the levels of NO_x in the gas phase of the reactor were
90 monitored continuously every 10 seconds until reaching a steady state within few minutes
91 (Figure SI-2). Despite that NO₂ concentrations up to 40 ppbv were detected initially (first
92 30s), a background level of NO_x (<5 ppbv) was quickly reached. This production of NO₂
93 might possibly be due to IMD photolysis under indoor lighting during preparation and
94 handling of the solutions. During IMD irradiation, we have chosen to monitor NO_x levels in
95 the gas phase of the reactor at selected times and not continuously. After selected irradiation
96 times, the light was turned off and the outlet of the reactor connected to the NO_x analyzer.
97 NO_x were measured every 10 s for a period of 1-2 min at a flow rate of 0.7 L min⁻¹. The time
98 profile of NO_x concentrations shown in Figure SI-2 corresponds to the decay of NO_x level in
99 the reactor due to the dilution with clean air. The level of NO_x measured was relatively
100 constant at 1h, 2h, 4h and 6h of IMD irradiation, in accordance with a steady state regime.
101 The levels of NO_x generated were then obtained by integrating the time profiles of NO_x
102 concentrations. For calculating the yields of NO_x, the ratio of NO_x concentrations (ppbv)
103 were converted into molar by taking into account the gas phase volume of the reactor (450
104 mL). By measuring the converted quantity (in moles) of IMD during the irradiation period, it
105 was possible to calculate the molar yield for NO and NO₂.



106 **Figure 1.** Schematic representation of device 1 used to monitor NO_x formation upon
 107 irradiation of IMD solutions.

108 A second device, device 2, was used to monitor the formation of nitro and nitroso-derivatives.
 109 15 mL of solutions were placed in a cylindrical Pyrex reactor sealed with an air-tight silicon
 110 cap and surrounded by six fluorescent tubes (Sylvania F15W/BL 368), installed inside a
 111 custom-made cylindrical irradiation device. Solutions were not buffered, but pH was
 112 controlled during the reactions. The initial pH was 6.5 ± 0.3 and in the course of the reactions,
 113 pH laid above 5. In the case of IMD+resorcinol mixtures, aliquots were sampled after several
 114 selected irradiation times and the consumption profile of IMD and nitro- and nitroso-
 115 resorcinol were obtained. For IMD+phenol and IMD+tryptophane mixtures and experiments
 116 with nitrate/nitrite and NOM, aliquots were only sampled after 16 h of irradiation. Samples
 117 were analyzed by HPLC to monitor the loss of IMD and the probes and by UHPLC-HRMS to
 118 characterize photoproducts and estimate their levels. For the experiment at 10^{-5} M of IMD and
 119 10^{-4} M of resorcinol, 75 ml were irradiated by portions of 25 ml, and water was evaporated up
 120 to 6 ml using a rotavapor before further analyses. Experiments were done in duplicate or
 121 triplicate. **Analytical methods.** Absorption spectra were recorded using a Varian Cary 3
 122 spectrophotometer. IMD, phenol, resorcinol and L-tryptophan concentrations were monitored
 123 by HPLC (Waters Alliance 2695) equipped with a photodiode array detector (Waters 2996)
 124 and a EC150/4.6 Nucleodur 100-5 C₈ endcapped column. The HPLC conditions are presented
 125 in Table SI-1. was quantified using the same instrument after derivatization with DNPH.²⁹ 15

126 mL of derivatizing solution were prepared by mixing concentrated HCl, ultrapure water and
127 acetonitrile in the ratio 2:5:1. 50 μL of this solution were added to 5 mL of sample solution.
128 Derivatization reaction was completed in 5 min and HPLC analyses were run shortly after.
129 Calibration used derivatized NO_2^- solutions in the concentration range 10^{-6} - 10^{-5} M. All the
130 HPLC analyses were done in triplicate and presented data are the mean values obtained.
131 NO_3^- was measured by ionic chromatography on a Dionex ICS-5000⁺ using a column model
132 Dionex Ion Pack AS11 2mm \times 250mm; the flow was 0.25 mL.min⁻¹ and the mobile phase was
133 an aqueous solution of KOH at the concentration of 0.43 mM for the first 4.5 min followed by
134 a linear gradient up to 18 min of runtime by rising KOH concentration up to 11.70 mM. The
135 injection volume was 750 μL and the temperature of the column oven was set at 30°C.
136 External standards were prepared using NaNO_3 in the concentration range 50-200 $\mu\text{g}\cdot\text{L}^{-1}$.
137 Nitro and nitroso-derivatives of phenol, resorcinol and L-tryptophan were characterized and
138 their concentrations estimated by high resolution mass spectrometry (HRMS) performed on
139 an Orbitrap Q-Exactive (Thermo Scientific) coupled to an ultra-high performance liquid
140 chromatography system (UHPLC) Ultimate 3000 RSLC (Thermo Scientific). Due to the lack
141 available standards, desnitro-IMD and minor photoproducts were tentatively identified by
142 HRMS but quantification was not possible. Analyses were carried out both in negative (ESI^-)
143 and positive (ESI^+) electrospray modes. The column was the same column as for HPLC-UV.
144 The binary solvent system was composed of acetonitrile and acidified water using formic acid
145 at 40% and 60% respectively with a flow of 1.0 mL min⁻¹. Nitro and nitroso-phenols were
146 quantified by injection of external standards of 4-nitro and 4-nitroso-phenols at concentrations
147 varying from 5×10^{-7} to 4×10^{-6} M (Figure SI-3). Due to commercial unavailability of nitrated
148 derivatives, the concentrations of nitro and nitroso-resorcinols were estimated using the
149 calibration curves of 4-nitro and 4-nitroso-phenols. The concentrations of nitro-tryptophan
150 and nitroso-tryptophan were estimated using L-tryptophan at the concentration of 10^{-6} M as a

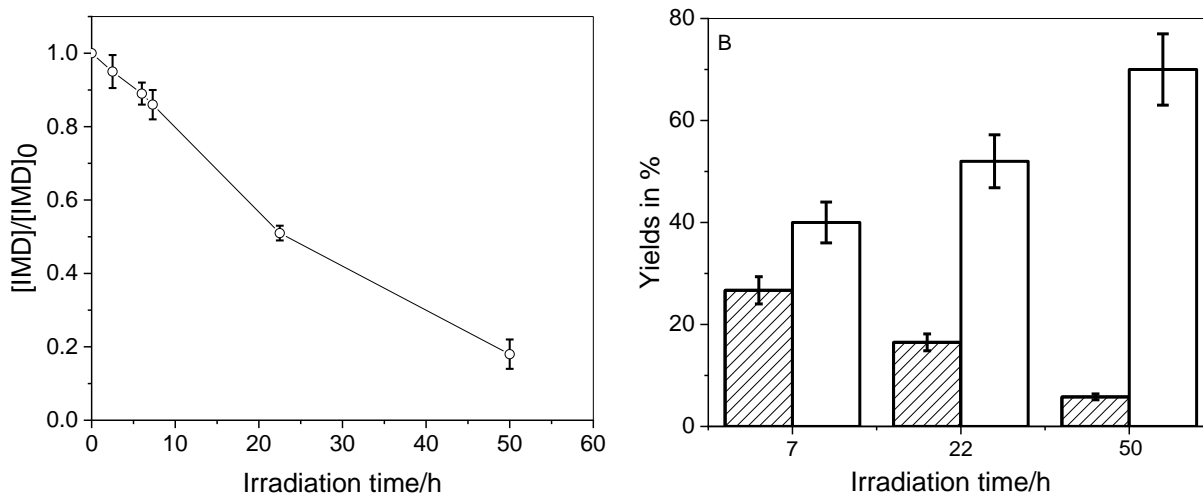
151 reference. Yields were obtained by dividing the photoproducts concentrations by the loss of
152 IMD in concentration and by multiplying these ratios by 100.

153 **Computational Method.** Potential Energy Surfaces (PES) were investigated with the
154 Gaussian series of programs.³⁰ Density Functional Theory (DFT) calculations (optimizations,
155 frequency calculations, identification of transition states and IRC calculations) were
156 performed at the MN12SX/6-311++G(d,p)//MN12SX/6-31+G(d,p) level of calculation.
157 Among the large set of hybrid range-separated functionals that we tested, MN12SX³¹ gave the
158 best agreement between experimental and theoretical absorption spectra. Finally, the time
159 dependent-DFT (TD-DFT) method was used to compute singlet excited states. Triplet state
160 was explored with conventional self-consistent field calculations. Solvent was modeled
161 implicitly with the Polarizable Continuum Model (PCM). Electronic energies are reported
162 throughout (Gibb's free energies are not provided here because low vibrational modes may
163 introduce large uncertainties in this calculation).

164

165 **RESULTS AND DISCUSSION**

166 **Photolysis of IMD.** The degradation profile of neutral aqueous IMD (10^{-4} M) irradiated in
167 device 1 is shown in Figure 2. HPLC-UV and UPLC-HRMS analyses indicated that the main
168 photoproduct was desnitro-IMD (Figure SI-4). Three minor photoproducts were also found: a
169 compound produced by addition of an oxygen atom on IMD (IMD+O), another one produced
170 by addition of two oxygen atoms on desnitro-IMD (desnitro-IMD+2O) and the nitroso
171 derivative of IMD (IMD-O) as traces (Table SI-2).

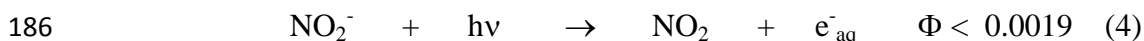
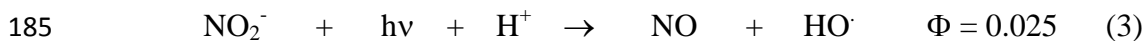
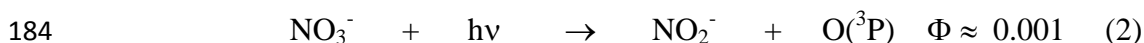
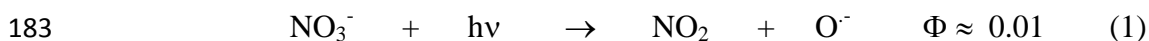


172

173 **Figure 2.** Consumption profile of aqueous IMD (10⁻⁴ M) irradiated in device 1 (A) and yields
 174 of NO₃⁻ (white bars) and NO₂⁻ (shaded bars) (B).). Error bars are standard deviations.

175

176 NO₃⁻ and NO₂⁻ were detected in the aqueous phase (Figure SI-4). The yield of NO₃⁻ increased
 177 constantly to reach 72±5% after 50 h of irradiation (Figure 2B, white bars). In contrast, the
 178 yield of NO₂⁻ decreased from 27% after 7 h of irradiation to 6% after 50 h (Figure 2B, shaded
 179 bars). The higher accumulation of NO₃⁻ compared to that of NO₂⁻ is consistent with the
 180 spectral properties and the known photoreactivity of these ions. NO₃⁻ (λ_{max}= 300 nm and ε= 8
 181 M⁻¹.cm⁻¹) absorbs much less solar light than NO₂⁻ (λ_{max}= 355 nm and ε= 22 M⁻¹.cm⁻¹) and its
 182 quantum yield of photolysis is also lower (reactions 1-4) leading to a smaller photolysis rate³²:



187

188 The detection of IMD+O and of desnitro-IMD+2O appear to be consistent with the formation
 189 of hydroxyl radicals through reactions (1) and (3).

190

191 **NO_x formation upon irradiation of IMD.** We also measured the NO_x formation in the
 192 gaseous phase above the solutions. NO and NO₂ were successfully detected upon irradiation
 193 of IMD (10⁻⁴ M) in device 1. Examples of collected data are shown in Figure SI-2. During the
 194 first two hours of reaction of irradiation, 24 μg of NO₂ and 0.88 μg of NO were produced
 195 whereas IMD loss was around 380 μg (See Table 2). After integrating nitrite and nitrate levels
 196 produced and considering the volume of gas (200 mL) and of water (450 mL), an overall mass
 197 balance of IMD conversion into inorganic N-containing products was determined: 40±8% for
 198 NO₂, 2±0.5% for NO, 52±5% for nitrate and 16±2% for nitrite.

199 **Table 2.** Formation of NO_x after 2 h of irradiation of IMD (10⁻⁴ M) or mixtures NO₃⁻/NO₂⁻ in
 200 device 1.

Conditions	Quantity of IMD converted	Quantity of NO ₂ formed (molar yield)	Quantity of NO formed (molar yield)
IMD (10 ⁻⁴ M)	380±20 μg	24±5 μg (40±8%)	0.88±0.20 μg (2±0.5%)
NO ₃ ⁻ (1.8×10 ⁻⁶ M)			
+		1.6±0.3 μg	3.9±0.8 μg
NO ₂ ⁻ (1.7×10 ⁻⁶ M)			
NO ₃ ⁻ (2×10 ⁻⁵ M)			
+		4.8±1.0 μg	11.6±2.3 μg
NO ₂ ⁻ (5×10 ⁻⁶ M)			

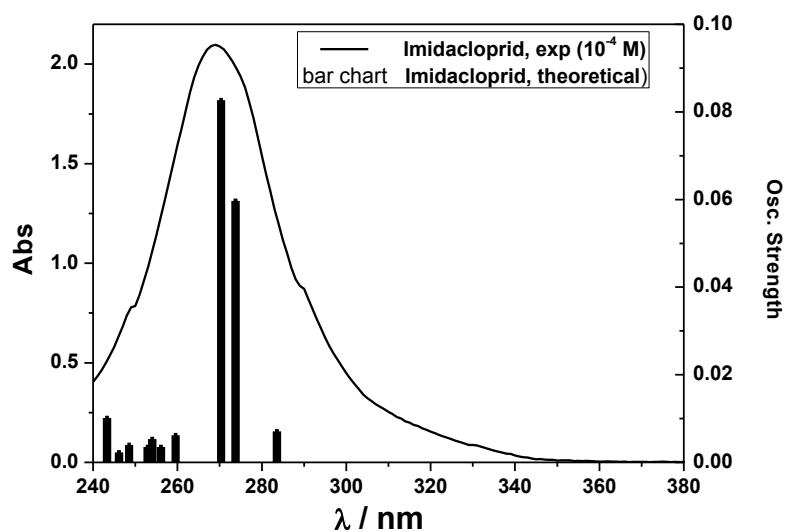
201 As the presence of $\text{NO}_3^-/\text{NO}_2^-$ in the aqueous solution could potentially generate NO_x ³³, we
202 irradiated these ions independently to estimate their contribution to the pool of NO_x detected
203 upon irradiation of IMD. We chose to perform these comparative experiments with $\text{NO}_3^- =$
204 1.8×10^{-6} M and $\text{NO}_2^- = 1.7 \times 10^{-6}$ M corresponding to the concentrations estimated after 2 h of
205 irradiation in device 1 (Figure SI-4). The irradiation of this mixture for 2 h yielded 15-fold
206 less NO_2 and 4.4-fold more NO than the irradiation of IMD (10^{-4} M) (Table 2). The amount of
207 NO_x formed above the IMD solution was 4.5-fold higher than that above the $\text{NO}_3^-/\text{NO}_2^-$
208 solution showing that IMD was the main contributor. Moreover, the higher yield of NO in the
209 latter system confirmed that the NO_x precursor in the $\text{NO}_3^-/\text{NO}_2^-$ mixture was NO_2^- through
210 reaction (3). At higher concentrations of $\text{NO}_3^-/\text{NO}_2^-$ (2.0×10^{-5} M and 5×10^{-6} M, respectively)
211 not far from those reached after 16h of IMD irradiation, NO and NO_2 levels were 3-fold
212 higher than in the previous case, respectively, showing that, in this concentration range, the
213 NO and NO_2 amounts accumulated proportionally to NO_2^- concentration. Again, the amount
214 of NO_x generated from NO_2^- (2.0×10^{-5} M) was still below the one formed upon irradiation of
215 IMD solution.

216 As previously shown, the bond N- NO_2 was cleaved when IMD was irradiated in the solid
217 phase at 305 nm and 254 nm.¹⁷ However, some questions remain unanswered: would the
218 proposed mechanism in the solid phase and at short wavelength be still valid in solution and
219 at longer wavelength, and thus at lower excitation energy? How is NO formed and how the
220 oxygen atom is eliminated? In an attempt to answer these questions, we performed quantum
221 calculations.

222

223 **Theoretical Calculations.** Several conformers were found for the solvated imidacloprid
224 system. The structure of the global minimum was similar to that found from recent first-
225 principles^{17,34} and crystallographic investigations³⁴ (see SI section for all structures reported in
226 this work). Moreover, the DFT method used here was able to reproduce accurately the
227 experimental absorption spectrum (see Figure 3).

228



229

230 **Figure 3.** Experimental (Abs, left axis) and theoretical (oscillator strengths, right axis)

231 absorption spectra of imidacloprid (theoretical spectrum for the most stable conformer (Fig.

232 SI-5a) at the TD-MN12SX/6-311++G(d,p),PCM//MN12SX/6-31+G(d,p),PCM level. The

233 oscillator strength is the probability of absorption. It is related to the dipole strength of the

234 transition and is proportional to the molar absorptivity maximum for this transition. The S_1 - S_0

235 transition is optically active (284 nm). The oscillator strength of this transition is 0.02 which

236 is significant (an ϵ of about $6000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ can be estimated from this value when a UV-

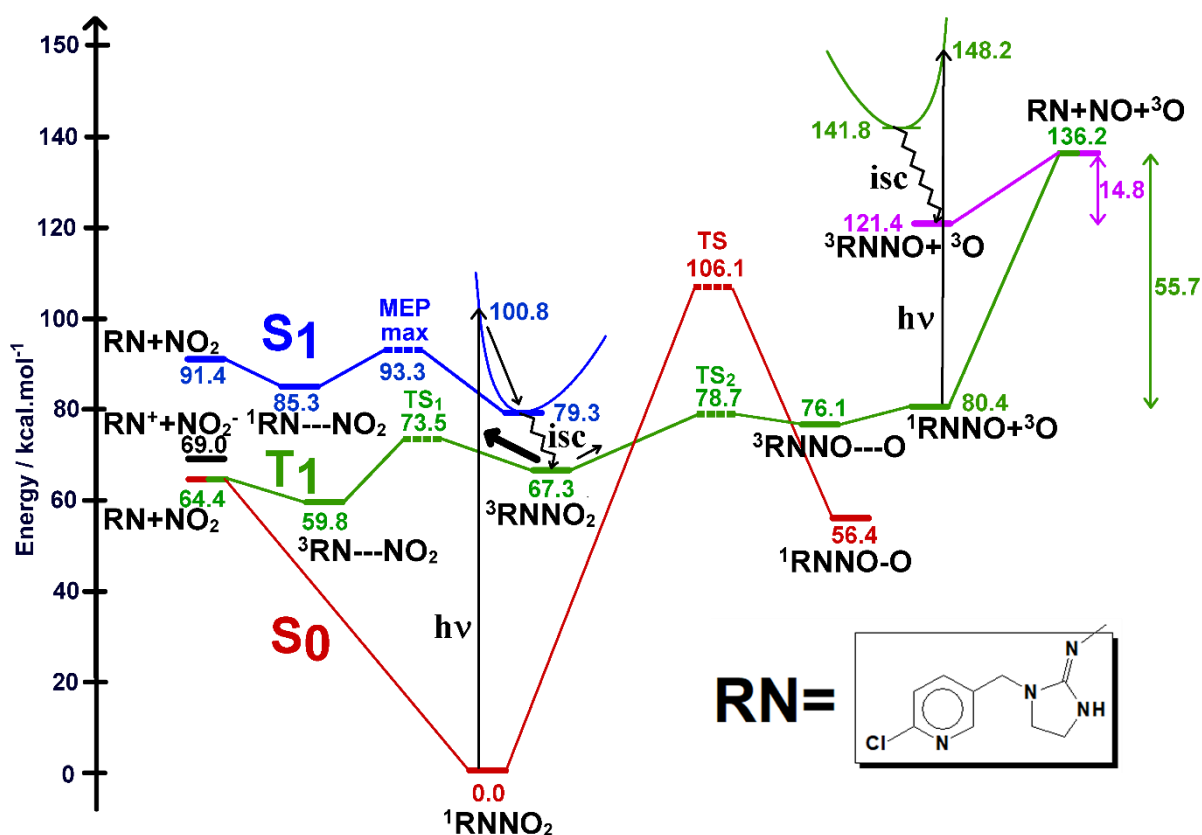
237 Vis Half-Width at half-height of 0.333 eV is used to model the absorption spectrum).

238

239 Detailed investigation of the ground state (S_0), first triplet state (T_1) and first singlet excited

240 state (S_1) was performed. Some of the key results are shown in Figure 4 and discussed below.

241 Minima and transition state structures are given in the SI section. The dissociation pathways
 242 of interest are depicted in this Figure: NO₂ is obtained in the left-hand side of Figure 4, and
 243 triplet atomic oxygen (a reaction that is precursor to the production of NO) is shown on the
 244 right-hand side of Figure 4. The Minimum Energy Path was followed to investigate the
 245 formation of NO₂ in S₁ by performing partial optimizations of imidacloprid for fixed RN-NO₂
 246 bond distances. The MEP maximum is indicated by a dashed level in Figure 4.
 247



248
 249 **Figure 4.** The electronic energies of stationary points in the ground state (S₀, red), first triplet
 250 (T₁, green) and first singlet (S₁, blue) excited states of imidacloprid (¹RNNO₂). Calculations
 251 were performed with the MN12SX/6-311++G(d,p),PCM//MN12SX/6-31+G(d,p),PCM
 252 method. Transition states and the MEP maximum are represented with dashed levels. Dashed
 253 bonds represent long-range separations. The energies of separated fragments RN+NO₂ and

254 ${}^1\text{RNNO}+{}^3\text{O}$ are also given in this Figure. The energy of the heterolytic dissociation products
255 (left-hand side, black) and the triplet state of RNNO (right-hand side, purple) are also
256 indicated. The separated fragments RN and NO_2 in S_1 are respectively in the first doublet
257 excited state (RN) and doublet ground state (NO_2).

258

259 S_0 and S_1 states. Our results show that departure of atomic triplet oxygen is not favored in the
260 ground state because the predissociated intermediate ${}^1\text{RNNO-O}$ ($\text{R(O-O)}=1.523 \text{ \AA}$; 56.4
261 kcal.mol^{-1}) cannot be reached due to very large activation energy ($106.1 \text{ kcal.mol}^{-1}$).
262 Similarly, the formation of NO_2 is not expected in the ground state because the respective
263 electronic dissociation energy in S_0 is large ($64.4 \text{ kcal.mol}^{-1}$; $\text{RN}+\text{NO}_2$). A transition state
264 could not be found between imidacloprid (${}^1\text{RNNO}_2$) and separated radicals in S_0 . This is
265 expected for homolytic dissociations in the ground state. In S_1 , the dissociation of the RN-
266 NO_2 bond required $14.0 \text{ kcal.mol}^{-1}$ (MEP maximum). In addition, the in-cage dissociation
267 complex ${}^1\text{RN--NO}_2$ is less stable ($85.3 \text{ kcal.mol}^{-1}$) than the respective reactant ($79.3 \text{ kcal.mol}^{-1}$).
268 Thus, dissociation in S_1 is less favored than that in the triplet state (an activation energy of
269 $6.1 \text{ kcal.mol}^{-1}$ was found in T_1 and the reaction is now exothermic; see Figure 4). Moreover,
270 our results show that the heterolytic dissociation mechanism would lead to species $\text{RN}^+/\text{NO}_2^-$
271 that are slightly less stable (see also SI) than the respective separated radicals (RN/NO_2).
272 Thus, it seems reasonable to consider that it is the radicals that are eventually obtained in the
273 liquid phase. However, considering the small energy difference between heterolytic and
274 homolytic dissociation energies, a mixture of homolytic and heterolytic dissociation products
275 might not be completely ruled out. Implicit solvation models underestimate the solvation free
276 energy of small ions, the cases of the proton and hydroxide being emblematic of this issue. In
277 order to address this point, we computed $\Delta G^*_{\text{r,calc}}$ the dissociation Gibbs free energy for both
278 heterolytic and homolytic NO_2 cleavage. In this calculation, $\text{RT}\times\ln(24.46)$ was added to

279 $\Delta G_{r,calc}^*$ to account for the free energy change of 1 mol of an ideal gas from 1 atm to 1M.³⁵
280 $\Delta G_{r,calc}^0 = \Delta G_{r,calc}^* + RT \times \ln(24.46)$ was 58.6 and 49.2 kcal.mol⁻¹ for, respectively, the
281 heterolytic and homolytic dissociation reactions, thus a difference of 9.4 kcal.mol⁻¹ (recall that
282 the respective difference of electronic energies was smaller, i.e. 4.6 kcal.mol⁻¹). Considering
283 the implicit solvation model may underestimate the solvation free energy for NO₂⁻ by as much
284 as 10 kcal.mol⁻¹, the radical dissociated species are still more stable than the heterolytic
285 dissociation fragments, in agreement with our results.

286

287 *Triplet State T₁*. Second, S₁/T₁ intersystem-crossing (*isc*) is favored because minimum
288 energy geometries in S₁ and T₁ are very similar for **RNNO₂** and the energy gap is small (less
289 than 0.1 kcal.mol⁻¹ at the Franck-Condon geometry). In addition, in the triplet state, the barrier
290 for **NO₂** dissociation (6.1 kcal.mol⁻¹) is significantly smaller than that for the dissociation into
291 triplet atomic oxygen and singlet fragment (¹**RNNO**+³**O**; 11.4 kcal.mol⁻¹), in agreement with
292 our experimental findings. Moreover, the in-cage dissociation complex ³**RNNO--O** is
293 thermodynamically less stable than the respective reactant ³**RNNO₂** and this reaction is
294 displaced toward the reactant. Nevertheless, this pathway was investigated below to see if this
295 reaction could play a role, even minor, in the formation of NO radicals.

296

297 *NO formation, a minor pathway*. The mechanism for production of nitric oxide from
298 ¹**RNNO** is also shown in Figure 4. NO bond dissociation energy was 55.7 kcal.mol⁻¹ for
299 ¹**RNNO** in the ground state, whereas cleavage in the triplet state (reached through S₁ followed
300 by *isc*) required only 14.8 kcal.mol⁻¹ (**RN** is obtained). A transition state could not be found in
301 T₁, and the energy of activation may be identified with the dissociation energy in that case.
302 Thus, the formation of NO as a primary product from RNNO is probably a minor pathway.

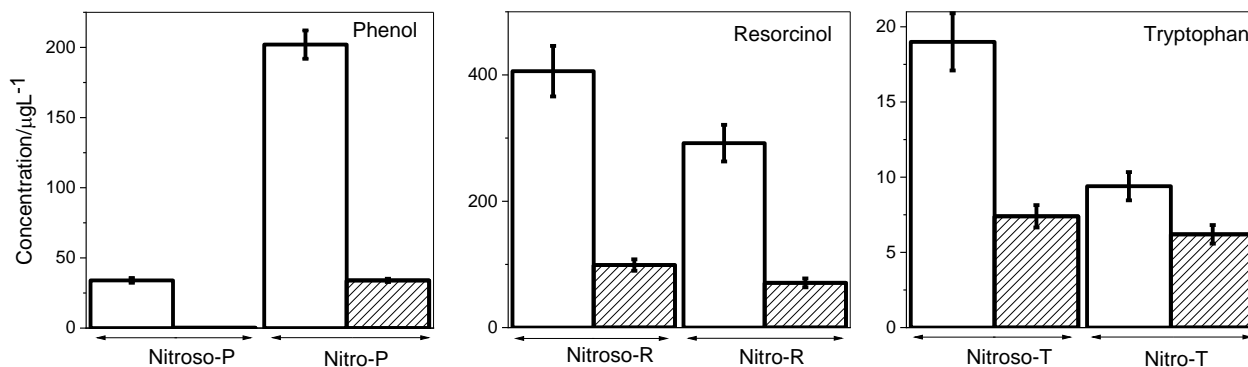
303 Thus, our quantum calculations provide strong evidence that photolysis of IMD mainly leads
304 to NO₂ formation in the overall triplet state potential energy surface while NO formation is a
305 minor pathway.

306

307 **Evidence of nitro/nitroso derivatives formation.** Nitrate and nitrite ions which generate HO·
308 radicals simultaneously with NO or NO₂ have been reported to photoinduce the nitration
309 and/or the nitrosation of phenolic derivatives.²⁰⁻²⁴ Whether the photolysis of IMD could also
310 contribute to the formation of such toxic products was a hypothesis that we aimed to verify in
311 this study. Thus, IMD was irradiated with each of the three probes shown in Scheme 2 in a
312 small reactor (device 2) for 16 h. In these conditions, the loss of IMD irradiated alone reached
313 60% (Figure SI-7). We first compared the probes consumption (10⁻⁴ M) in the absence and in
314 the presence of IMD (10⁻⁴ M) to quantify the photoinductive effect (Table SI-4). The
315 disappearance of phenol and resorcinol were drastically faster in the presence of IMD,
316 evidencing a strong effect. Only in the case of tryptophan, the acceleration effect was small
317 due to the fast photolysis of the probe under the studied conditions.

318 Then, we monitored the formation of nitro/nitroso-derivatives by UHPLC-HRMS analyses.
319 Figure SI-8 shows the formation profile of nitroso and nitro-resorcinol upon irradiation of
320 IMD (10⁻⁴ M) and resorcinol (10⁻⁴ M). The concentration of the two photoproducts increased
321 linearly up to 7h of irradiation before reaching a plateau value after 16 h. Nitro and nitroso-
322 derivatives were also detected with phenol and tryptophan. Detected levels after 16h of
323 irradiation are given in Figure 5 (white bars) and Table SI-4. The estimated yields of nitro-
324 resorcinols reached 3.3% of converted IMD and that of nitroso-resorcinols 5.1%. The yield of
325 nitro-phenols (*ortho+para* derivatives)²¹ was equal to 2.6% and that of nitroso-phenols
326 (*ortho+para* derivatives) smaller (0.5%). For tryptophan, both yields were very small,

327 reaching only 0.08% (nitro-derivatives) and 0.14% (nitroso-derivatives) of tryptophan
328 converted, due to the fast direct photolysis of tryptophan.



329

330 **Figure 5.** Concentrations of nitro and nitroso-derivatives of phenol, resorcinol and tryptophan
331 detected after 16 h of irradiation of the probes (10⁻⁴ M) in device 2 in the presence of IMD
332 (10⁻⁴ M) (white bars) and in presence of the mixture of NO₃⁻ (2×10⁻⁵ M) and NO₂⁻ (5×10⁻⁶ M)
333 (shaded bars). Error bars are standard deviations.

334 Experiments were also performed at lower reactants concentrations to determine the impact of
335 this parameter on the rates. A 10-fold decrease of the concentration of IMD for a
336 concentration of resorcinol kept constant at 10⁻⁴ M, reduced the amount of nitro-resorcinols by
337 18-fold and that of nitroso-resorcinols by 9-fold while the sum of the two photoproducts was
338 reduced by about 10-fold (Table SI-4). A 10-fold decrease of the concentration of resorcinol
339 for a concentration of IMD kept constant at 10⁻⁴ M, decreased 3-fold the amount of nitro-
340 resorcinols and 100-fold that of nitroso-resorcinols and the sum (nitro+nitroso) was reduced
341 by about 5-fold (Table SI-4). These results indicate that the reaction rate was proportional to
342 the concentrations of reactants. The decay rate of resorcinol followed a first order kinetic with
343 a rate constant k that can be expressed as : $k = 5.9 \times 10^{-3} [\text{IMD}] \text{ s}^{-1}$.

344 We also studied the nitro/nitrosation capacity of the $\text{NO}_3^-/\text{NO}_2^-$ mixture to quantify their
345 contributions in these reactions (shaded bars in Figure 5 and Table SI-4). For these
346 comparisons, we fixed $\text{NO}_3^-/\text{NO}_2^-$ concentrations to those measured in the IMD solution after
347 16h of irradiation in device 2 (2×10^{-5} M and 5×10^{-6} M, respectively) and the mixtures NO_3^-
348 $/\text{NO}_2^-$ + probes were irradiated for 16 h in device 2. Nitrosation was 121-fold lower in the
349 case of phenol, 4.1-fold in the case of resorcinol and 2.6-fold in the case of tryptophan than in
350 the presence of IMD while nitration was 5.9-fold lower for phenol, 4.1-fold for resorcinol and
351 1.5-fold for tryptophan. One concludes that the contributions of $\text{NO}_3^-/\text{NO}_2^-$ to the
352 nitration/nitrosation processes observed in irradiated IMD solutions were minor especially for
353 phenol and resorcinol even though we acknowledge that the conditions chosen for the
354 comparative experiments (fixed $\text{NO}_3^-/\text{NO}_2^-$ concentrations) cannot perfectly reproduce the
355 dynamic and complex evolution of $\text{NO}_3^-/\text{NO}_2^-$ during IMD irradiation.

356

357 **Effect of NOM on nitration/nitrosation of probes.** Another important aspect we attempted
358 to explore is the effect of NOM on these photochemical nitration/nitrosation. Experimental
359 conditions and results are reported in Table 3. NOM (11 mg.L^{-1}) increased the percentage of
360 resorcinol loss in the presence of IMD by a factor of 2.6, after correction for the light
361 screening effects (10%). The formation of nitroso and nitro-resorcinols in IMD solutions were
362 increased by a factor of 1.3 and 2.0, respectively, and the formation of nitro and nitroso-
363 resorcinols in NO_2^- solutions by factors of 35 and 2.8, respectively. The very low formation of
364 nitro-resorcinols in the system NO_2^- +resorcinol was already shown.²⁰ These data highlight
365 the significant effect of NOM on the nitro/nitroso-derivatives formation.

366

367 **Table 3.** Effect of NOM (11 mg.L⁻¹) on the photo-nitration/photo-nitrosation of resorcinol
 368 (10⁻⁴ M) after 2 h of irradiation in device 2 in the presence of IMD (10⁻⁴ M) or NO₂⁻ (5×10⁻⁶
 369 M). The light screening effect of NOM (10%) is taken into account.

Conditions	% resorcinol converted	Nitroso- derivatives formed (μg.L ⁻¹)	Nitro- derivatives formed (μg.L ⁻¹)
IMD +resorcinol	7.0±0.3	83±8	44±4
IMD +resorcinol+NOM	18±1	110±10	88±9
NO₂⁻ +resorcinol	< 1	20±2	1±0.1
NO₂⁻ +resorcinol+NOM	< 1	55±5	35±3

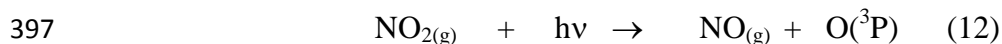
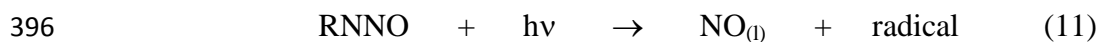
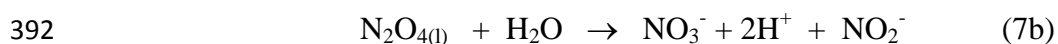
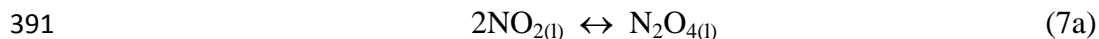
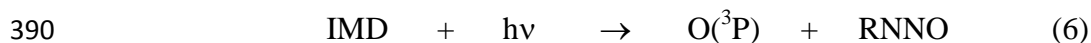
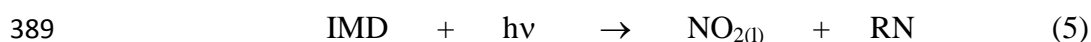
370

371 **Reaction mechanism.** Many reactions are expected to take place in this complex system. The
 372 main ones are summarized below. The photolysis of IMD in water generates NO₂ in the liquid
 373 phase (NO_{2(l)}) together with the radical RN as shown by the quantum calculations and this
 374 latter gives rise mainly to desnitro-IMD (reaction 5). The radicals O(³P) and RNNO are also
 375 produced but in much lower amounts (reaction 6). The reactivity of NO₂ in water is very high.
 376 It is reported in the literature that NO₃⁻ and NO₂⁻ are generated according reactions (7a and 7b)
 377 through the intermediary dimerisation of NO_{2(l)}.^{36,37} NO₃⁻ and NO (NO_(l)) can also be
 378 produced through reaction (8).^{37,38} In our experiments, N₂O_{4(g)} cannot be distinguished from

379 $\text{NO}_{2(g)}$. Reaction (8) is probably the major NO formation pathway, but the photolysis of
 380 RNNO (reaction 11), of $\text{NO}_{2(g)}$ (reaction 12) and of NO_2^- (reaction 3) are alternative pathways
 381 for NO formation. NO is stable in water and volatilizes in the gaseous phase (reaction 9).³⁷ It
 382 generates $\text{NO}_{2(g)}$ by reaction with oxygen (reaction 10).

383 In this scheme, we did not take into account the oxidation of IMD by HO^\bullet formed in reaction
 384 (3) because the formation of oxidation products (IMD+O) was small. NO_2^- and NO_3^- could be
 385 also oxidized by HO^\bullet .³⁹ However, due to the high concentration of IMD compared to those of
 386 NO_2^- and NO_3^- in the first half of the reaction, IMD and its main photoproduct desnitro-IMD
 387 are expected to be the main sinks of HO^\bullet .

388



398

399 The nitration/nitrosation of phenolic/aromatic compounds in the presence of NO_2^- or NO_3^- has
 400 been already studied.^{20-25,39-41} NO_2 is recognized as having a key role in these reactions, even
 401 though the mechanisms are not fully understood. Several studies attributed the formation of
 402 phenoxy radicals to the reaction of phenols with NO_2 ^{20,25,39,41} while others to their reaction

403 with HO[·] ⁴⁰. Once formed phenoxyl radicals further react NO₂ to yield the ortho and para
404 derivatives of nitro-phenols. Similarly, the reaction of phenoxyl radicals with NO are
405 expected to generate nitroso-phenols. The effect of NOM on these reactions is difficult to
406 predict due to the existence of opposite reactions. Indeed, on the first hand, NOM can
407 potentially favor nitro/nitrosation reactions by generating photooxidants such as triplet excited
408 states (³NOM*), singlet oxygen or HO[·] that are expected to induce the formation of phenoxyl
409 radicals as shown in the literature.³⁹ In addition, ³NOM* or HO[·] could be able to oxidize NO₂⁻
410 and NO₃⁻ into NOx³⁹ (see process 13 related to NO₂⁻):

411



413

414 On the other hand, NOM could be also a sink for NOx due to the presence of aromatic
415 moieties in its structure and therefore could inhibit the nitration/nitrosation reaction to some
416 extent.^{26,42} The overall effect of NOM will thus depend on the experimental conditions and in
417 particular on the relative concentrations of reactants. In our set-up, the presence of NOM (11
418 mg.L⁻¹) in IMD or NO₂⁻ solutions containing resorcinol (10⁻⁴ M) increased the amounts of
419 nitro and nitroso-resorcinols showing that in this case NOM favors the formation of the
420 phenoxyl radical and of NO₂. Since Suwannee River NOM contains 68% of fulvic acids and
421 fulvic acids contain ~3 mmol oxidizable phenol per g of carbon⁴³, there are about 20 μM of
422 oxidizable phenols originating from NOM in a solution containing 11 mg/l. Under these
423 conditions where the quenching molecule is in large excess over phenolic moieties in NOM, it
424 can be expected that the majority of NOM-derived photooxidants will be quenched by the
425 probe compounds to form phenoxyl radicals, which can then further react with NOx to
426 produce nitro/nitroso-phenol/resorcinol, enhancing the yields of these products as it is
427 observed.

428

429 **Environmental significance.** Our study showed that NO_x (NO and NO₂) could be generated
430 by irradiation of IMD and that these NO_x were capable of reacting with phenolic probes to
431 produce nitro and nitroso-derivatives. This suggests that in surface water, IMD could induce
432 the formation of nitro and nitroso derivatives of other contaminants that could be toxicants in
433 the aquatic environment. The importance of the phenomenon will depend on the level of IMD
434 present in surface waters. The frequency of IMD detection in surface waters is high and
435 concentration of IMD varies in a large range reaching 1 µg.L⁻¹ in agricultural areas.^{3,4} Based
436 on this work and on the light absorption capacities of IMD and NO₂⁻, one can calculate that at
437 1 µg.L⁻¹, IMD could generate as much as nitroso/nitro-derivatives as NO₂⁻ at 0.1 µg.L⁻¹. The
438 relative contributions of NO₂⁻ and IMD to nitroso/nitro-derivatives formation depend
439 therefore on their levels in water. NO₂⁻ is present in surface waters at a maximal concentration
440 of 0.1 mg.L⁻¹.⁴⁴ In many cases, NO₂⁻ concentration will be high enough to make negligible
441 the contribution of IMD in nitro/nitrosation reactions. However, in waters containing very low
442 levels of NO₂⁻ and high levels of IMD, IMD might play a role in the nitro/nitrosation
443 reactions.

444 On the other hand, we observed that NOM (11 mg.L⁻¹) enhanced nitro and nitrosation
445 reactions of phenols (10⁻⁴ M). The yield of nitro-resorcinol was multiplied by 2 whereas that
446 of nitroso-resorcinol by 1.3 and when NO₂⁻ was used instead of IMD, the yields of nitro-
447 resorcinol and of nitroso-resorcinol were 35-fold and 2.8-fold increased respectively. This can
448 be explained by the enhanced formation of phenoxy radicals in the quenching of NOM
449 deriving photooxidants by phenols. However, this effect might be concentration-dependent.
450 The level of NOM used in this study falls in the range of typical NOM levels found in rivers
451 and eutrophic lakes⁴⁵, but those of probes are high. At environmentally relevant
452 concentrations of the probe compounds (<1 µM), phenolic moieties in NOM are in excess and

453 it might be possible that the NOM-bound phenoxy radicals, in higher concentration than
454 probe -derived phenoxy radicals might outcompete the latter for reaction with NO_x. In other
455 words, at environmentally relevant conditions, a shift towards nitration/nitrosation of NOM
456 seems possible and the yield of nitro/nitroso-derivatives of probes could then be lower
457 compared to the ones in the absence of NOM. The incorporation of N inorganic nitrogen (N)
458 into NOM *via* photolysis of nitrate/nitrite and/or in advanced oxidation processes treatments
459 was already reported and shown to generate also potentially toxic compounds.²⁶⁻²⁸ Therefore
460 such reactions might have also environmentally negative consequences. We could not detect
461 any significant structural changes in NOM using HRMS analyses. Nevertheless, further
462 experiments using N-labelled IMD or nitrite/nitrate and other hyphenated techniques may
463 provide evidence of NOM nitration/nitrosation. Therefore, a consistent monitoring of
464 nitro/nitroso byproducts is highly recommended to verify their potential formation.

465 Our study confirms the capacity of water contaminants to interact with each other under
466 irradiation and to induce mutual degradation. Mutual effects can involve reactions between
467 excited and ground states contaminants or the intermediary formation of reactive species like
468 NO_x in the case of IMD. Up to now, they have been poorly investigated in photochemical
469 studies and would deserve more attention. Thus, future studies should further consider the
470 investigation of the “cocktail effect” on the environmental fate of contaminants and more
471 specifically the reactivity of intermediates in order to enable a more reliable monitoring of
472 non-target pollutants and assessment of potential risks.

473

474 **ASSOCIATED CONTENTS**

475 **Supporting information:**

476 15 pages, 8 Figures and 4 Tables

477 Spectrum of light received by the solutions in devices 1 and 2. NO_x formation in device 1
478 upon photolysis of IMD (10⁻⁴ M). Calibration curve for nitroso-phenol and for nitro-phenol.
479 Profile of NO_x, NO₃⁻, NO₂⁻, nitroso-resorcinol and nitro-resorcinol formations and of IMD
480 consumption. Structure and cartesian coordinates of the minimum energy structures of IMD in
481 S₀ (a), S₁ (b) and T₁ (c), the TS (d), intermediate RNNO-O (e) in S₀, TS₁ in T₁ (f), TS₂ in T₁
482 (g), ³RN-NO₂ (h), ³RN-NO₂ in T₁ (i), ¹RNNO (j) and ³RNNO (k) at the B3LYP/6-
483 311++G(d,p)//B3LYP/6-31+G(d,p) level. Minima and transition state structures with
484 cartesian coordinates. Photo-nitration and photo-nitrosation of the probes after 16 h of
485 irradiation in presence of IMD (10⁻⁵ or 10⁻⁴ M) or a mixture of NO₃⁻ (2×10⁻⁵ M) and NO₂⁻
486 (5×10⁻⁶ M). Effect of NOM (11 mg L⁻¹) on the photo-nitration/photo-nitrosation of resorcinol
487 (10⁻⁴ M) after 2 h of irradiation in device 2 in the presence of IMD (10⁻⁴ M) or NO₂⁻ (5×10⁻⁶
488 M).

489

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499

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