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# 1 **Indoor heterogeneous photochemistry of furfural drives emissions of nitrous acid**

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4 France.

## 5 **Abstract**

6 People spend approximately 80% of their time indoor, making the understanding of the indoor  
7 chemistry an important task for safety. The high surface-area-to-volume ratio characteristic of  
8 indoor environments leads the semi-volatile organic compounds (sVOCs) to deposit on the  
9 surfaces. Using a long path absorption photometer (LOPAP), this work investigates the  
10 formation of nitrous acid (HONO) through the photochemistry of adsorbed nitrate anions and  
11 its enhancement by the presence of furfural. Using a high-resolution proton transfer reaction-  
12 time of flight-mass spectrometer (PTR-TOF-MS), this work also investigates the surface  
13 emissions of VOCs from irradiated films of furfural and a mix of furfural and nitrate anions.  
14 Among the emitted VOCs, 2(5H)-furanone/2-Butenedial was observed at high concentrations,  
15 leading to maleic anhydride formation after UV irradiation. Moreover, the addition of  
16 potassium nitrate to the film formed NO<sub>x</sub> and HONO concentrations up to 10 ppb, which scales  
17 to ca. 4 ppb for realistic indoor conditions. This work helps to understand the high levels of  
18 HONO and NO<sub>x</sub> measured indoors.

19

## 20 **Keywords**

21 Indoor air quality, Furfural, Nitrous Acid, Surface reaction, Photochemistry

22

23

24 **Practical implications**

25 Furfural is a ubiquitous pollutant indoors, which in the adsorbed state, induces photochemical  
26 properties to indoor surfaces. This photochemistry is shown here to significantly enhance the  
27 formation of nitrous acid and therefore impact the oxidation capacity indoors.

## 28 1. Introduction

29 Current atmospheric chemistry knowledge, built over the last decades, was found to be  
30 insufficient when applied to indoor air chemistry<sup>1</sup>. The indoor environment is a complex mix  
31 of sources and sinks due to biogenic, human and microbial activities under unique conditions  
32 (e.g., light, humidity and temperature)<sup>2,3</sup>. For instance, volatile organic compounds (VOCs) are  
33 often present in higher concentrations indoors than outside, affecting its air quality<sup>4-7</sup>. Furfural  
34 is a VOC emitted from multiple materials, generally produced under thermal stress from the  
35 degradation of polyoses (hemicelluloses)<sup>3,8,9</sup> through a mechanism previously described<sup>10</sup>.  
36 Furfural is expected to be present indoor, emitted from surfaces of wood based products<sup>11</sup> which  
37 are known to be an important source of indoor pollutants<sup>12</sup>. Concentrations measured in Italy  
38 and Finland reveal average levels of few  $\mu\text{g m}^{-3}$  with levels reaching up to  $39 \mu\text{g m}^{-3}$ <sup>9,13,14</sup> in  
39 homes, offices and public buildings, and was observed in dust in houses at about  $20 \mu\text{g g}^{-1}$ <sup>15</sup> in  
40 Sweden. Recently, experiments were conducted within the House Observations of Microbial  
41 and Environmental Chemistry, aiming to understand the indoor chemistry in the average US  
42 home. Average indoor concentration measured were similar to the concentrations observed in  
43 Europe at about  $4 \mu\text{g m}^{-3}$  and decreased by a factor 10 when the room was ventilated. The  
44 presence of furfural at comparable levels in Europe and the US highlights its importance  
45 independently of the architectural styles i.e., it is not limited to wooden houses. It was  
46 determined that the time required for the furfural to reach steady state concentration indoor is  
47 shorter than the average air renewable rate, indicating that surfaces act as an important reservoir  
48 of this VOC<sup>11</sup>. As high concentrations measured in some buildings can be linked to the presence  
49 of books and wooden furniture<sup>9,14</sup>, incense burning is also a major source of furfural leading to  
50 harmful concentrations of the order of magnitude of  $10^1 \text{ mg m}^{-3}$ <sup>16</sup>. The occupational exposure  
51 limit was set to  $8 \text{ mg m}^{-3}$  over a period of 8 hours<sup>17</sup>. Furfural is regarded as a key product in the  
52 chemical industries, hence its production was deeply researched in the 20<sup>th</sup> century<sup>18</sup>. It

53 currently has many uses in the industry as a solvent. It could also be used as a marker for indoor  
54 air quality control due to his abundance and volatility<sup>19</sup>.

55 Indoor surfaces are a medium where a wide range of compounds can react, offering a  
56 complex chemistry that can be affected by indoor light. While volatile compounds are rapidly  
57 ventilated out in most indoor environments, semi-volatile compounds (sVOCs) tend to adsorb  
58 on surfaces due to the high surface-area-to-volume ratios (ranging from 1 to 2 m<sup>2</sup> m<sup>-3</sup>)<sup>20,21</sup>, and  
59 are therefore sustained for longer times. It is acknowledged that ozone indoor is lost primarily  
60 through reactions on the surface leading to the formation of VOCs<sup>22</sup>. Other gas phase  
61 compounds can react on the surface such as NO<sub>2</sub> through hydrolysis<sup>23</sup> as well as HONO that  
62 can interact with indoor surfaces to produce hazardous compounds like nitrosamines<sup>24</sup>. In  
63 additions, nitric acid can be photolyzed when organic coating are present on the surface<sup>25</sup>.  
64 Surfaces with specific coatings such as paintings could also produce organic indoor air  
65 pollutants like VOCs, NO<sub>x</sub> and HONO when exposed to UV irradiation<sup>26-29</sup>. While indoor  
66 irradiation is less intense than outside and high energy wavelengths below 330 nm are scarce,  
67 photochemistry is still an important factor indoors<sup>30-34</sup>.

68 The hydroxyl radical (OH) was found to be a major indoor oxidant, which was thought to  
69 be mainly produced from the ozonolysis of unsaturated VOCs<sup>35</sup>. However, a recent study by  
70 Mendez et al.<sup>21</sup> showed that the photolysis of nitrous acid (HONO) can also be a significant  
71 source of OH radicals, contributing to more than 50% of their sources<sup>31,36</sup>. HONO can be  
72 produced heterogeneously through the processing of adsorbed nitrate anions or gaseous  
73 nitrogen oxides, which are ubiquitous indoors<sup>32,37</sup>. Arata et. al.<sup>38</sup> recently reported direct  
74 measurements of indoor N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub>, which can participate in reactions producing HNO<sub>3</sub>.  
75 Indoor nitric acid is not readily photolyzed and is likely to deposit onto surfaces, where water  
76 layers could lead to hydrolysis and production of surface nitrate. Nitrate was measured on  
77 indoor surfaces with concentrations varying from 10<sup>-3</sup> to 10<sup>-5</sup> mol m<sup>-2</sup><sup>39,40</sup>.

78 In this paper, the photochemistry of deposited furfural and its implication in converting  
79 nitrogen oxides or adsorbed nitrate anions into gaseous HONO and NO<sub>x</sub> were investigated  
80 through laboratory experiments. Furfural seems to be a ubiquitous VOC emitted from  
81 surfaces<sup>9,11,13,14</sup>, and here we suggest that its presence on these surfaces is conferring  
82 photosensitizing properties to them. Those properties are tested here by investigating the  
83 photoconversion of adsorbed nitrate to HONO, and the formation of surface peroxy radicals.  
84 This knowledge will lead to a better description of surface photochemistry indoors, and possibly  
85 closing a gap in our understanding of indoor HONO and hydroxyl radical formation.

## 86 **2. Materials and Methods**

87 As stated above, our aim is to explore the photosensitizing properties of adsorbed furfural  
88 representative of indoor wooden surfaces. We therefore prepared and exposed organic films  
89 made of deposited furfural, doped or not with nitrate anions, to light emitted from a LED in a  
90 small photo reactor described below. Gaseous products, including VOCs and HONO were  
91 monitored, and the production of surface peroxy radicals probed indirectly by their titration  
92 with NO.

### 93 ***2.1. Experimental protocol***

#### 94 ***2.1.1. Film preparation***

95 Aqueous solutions of furfural and potassium nitrate were prepared in Milli-Q water (18.2 MΩ  
96 cm) with concentrations varying from 0.01 M to 0.5 M and 0.01 mM to 1 M, respectively. Two  
97 mL of a fresh solution was evenly dispersed on a circular borosilicate glass window (50 mm  
98 diameter). The glass window was weighed before the preparation, dried over a period of 12  
99 hours in a desiccator filled with silica gel desiccant and placed in an oven at  $323.2 \pm 0.1$  K.  
100 Once dried, the glass windows were weighed again and used in an experiment within one day.

#### 101 ***2.1.2. Irradiation setup***

102 The organic films deposited on the glass substrates were placed at the bottom of a borosilicate  
103 glass reactor (height = 4 cm; volume = 80 cm<sup>3</sup>) and irradiated for 45 minutes (or more) using a  
104 LED lamp (M340L4; Thorlabs,  $\lambda_{\text{max}} = 345$  nm, nominal maximum irradiance 2.22 W/m<sup>2</sup>)  
105 placed 2 cm above the reactor. The humidity within the reactor was adjusted by varying the  
106 flows of synthetic air or synthetic N<sub>2</sub> passing through a bubbler or connected directly to the  
107 reactor.

108 This reactor was maintained at room temperature and flushed with nitrogen or synthetic air  
109 at a flow rate of 90 mL min<sup>-1</sup>. The outlet of the flow cell was connected to all the analytic  
110 devices described above.

111 For the experiments of NO uptake (section 3.4), a constant gas flow of nitric oxide at [NO]  
112 = 68 ± 2 ppb was used. To stabilize the NO concentration, the flow first bypassed the reactor  
113 and was then injected into the reactor at the beginning of the film exposure.

114

## 115 ***2.2. Analytical devices and protocols***

### 116 ***2.2.1. UV analysis***

117 The UV-vis absorption of the organic films in the range 200–600 nm by means of Cary 60 UV-  
118 Vis spectrophotometer (Agilent Technologies) in the liquid (after extraction) and solid  
119 (adsorbed) phases. The solid-liquid extraction was performed by rinsing the films with 2 mL of  
120 Milli-Q water. This solution which was then diluted between 2 and 20 times prior to be optically  
121 probed in 3500 µL Macro Fluorescence Cuvette (Thorlabs). The absorption of the solid films  
122 was simply probed by placing the circular borosilicate glass window on which the organic film  
123 was adsorbed perpendicularly to the optical beam within the spectrometer. Each analysis was  
124 performed on three different locations of the film and then averaged, and the absorbance from  
125 the glass window subtracted.

### 126 ***2.2.2. PTR-TOF-MS analysis***

127 In order to monitor the emissions of volatile organic compounds (VOC) from the furfural films,  
128 a proton transfer reaction-time of flight mass spectrometer (PTR-TOF-MS, 8000 - Ionicon  
129 Analytik GmbH, Innsbruck, Austria) was deployed, as described in detail by Ponczek and  
130 George<sup>24</sup>. This soft ionization procedure limits, while not preventing as discussed by Španěl et  
131 al.<sup>25</sup>, the fragmentation of the VOC to be analyzed and enables to the detection of a large number  
132 of compounds.

133 All PTR-TOF-MS measurements were performed using the H<sub>3</sub>O<sup>+</sup> ionization mode with the  
134 following parameters: source current of 4.0 mA, drift tube voltage of 600 V, drift tube  
135 temperature of 373 K, inlet temperature at 353 K and a drift pressure of 2.20 mbar. The E/N  
136 was about 123 Td. Spectra were collected at a time resolution of 10 s. Mass calibrations were  
137 performed using internal calibration based on two ions with known mass: hydronium ion  
138 isotope (H<sub>3</sub><sup>18</sup>O<sup>+</sup> m/z 21.022) and protonated acetone (C<sub>3</sub>H<sub>7</sub>O<sup>+</sup> m/z 59.049).

### 139 **2.2.3. High-resolution NMR analysis**

140 Characterization of the furfural films by <sup>1</sup>H NMR were carried out using a Bruker AVANCE  
141 HD (400 MHz) spectrometer equipped with a 5mm BBFO Z-gradient probe. The films were  
142 dissolved in 1 mL DMSO-d<sub>6</sub> and 600 μL of this solution was used for the NMR tube  
143 preparation. Quantitative <sup>1</sup>H NMR was carried out at a frequency of 400.13 MHz using a 30°  
144 flip angle (3.1 μs) with a recycle delay of 1 s and an acquisition time of 5 s. Sixteen scans of  
145 single pulse <sup>1</sup>H excitation were collected over a spectral width of 20 ppm. Data were acquired  
146 and processed with Bruker topspin 3.2 software.

### 147 **2.2.4. HONO and NO<sub>x</sub> gaseous analytics**

148 A Long Path Absorption Photometer (LOPAP, QUMA) was used to measure the concentrations  
149 of gaseous HONO<sup>23</sup>. In brief, HONO was sampled in a stripping coil by a fast-chemical reaction  
150 and converted into an azodye, which was photometrically detected in a long path absorption  
151 cell. The inlet gas flow was set to 500 mL min<sup>-1</sup> and the integrated time resolution was set at 7



152 min with a detection limit less than 10 ppt. The liquid flow used for the reactants was set to 20  
153 ml min<sup>-1</sup> and the sampling unit was maintained at 293 ± 0.02 K using a (Thermo Scientific  
154 ARCTIC Refrigerated/Heated Bath SC100 A10 - 230V), which was calibrated each week.

155 A standard chemiluminescence NO<sub>x</sub> analyzer (CLD 88 CY analyzer, Eco Physics) was used  
156 to monitor NO and NO<sub>2</sub> concentrations, with a detection limit of 50 ppt. In the first channel,  
157 NO reacts with O<sub>3</sub> to produce NO<sub>2</sub>\*, which emits a radiation ( $\lambda_{\text{max}} = 1200 \text{ nm}$ ) detected by a  
158 photomultiplier. A second canal allows NO<sub>2</sub> to be converted to NO using a reductor agent with  
159 a yield of 70%. The NO<sub>2</sub> concentration was obtained by calculating the difference measured  
160 between the two channels.

### 161 **2.3. Reagents**

162 Furfural (99%), potassium nitrate (≥99.0%) and dimethyl sulfoxide-d<sub>6</sub> (99.9%) were provided  
163 by Sigma Aldrich; NO (1 ppm in N<sub>2</sub>) was from Linde, synthetic air (>99.9%) was from Air  
164 Products and N<sub>2</sub> was synthetic (>99.9992%). The silica gel desiccant used was provided by  
165 Alfa Aesar (indicating, ACS, -4 + 10 Meh Granules) and Drying Pearls Orange was from Sigma  
166 Aldrich. The glass windows were made of borosilicate except one made of quartz and were  
167 used for the UV analyses of the films.

168

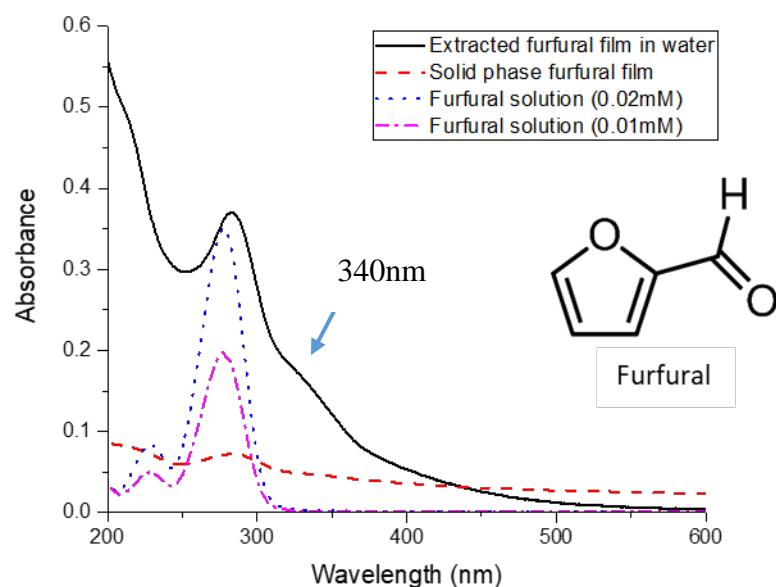
## 169 **3. Results and discussion**

### 170 **3.1. Film characterization**

171 During the film preparation, more than 99% of the mass of furfural was lost by evaporation of  
172 the product. For instance, after depositing 96.1 mg of furfural from 2 mL of a solution at 0.5  
173 M, only 0.7 ± 0.4 mg remained after the drying procedure. In other words, all the experiments  
174 were performed on very thin films made only from furfural residues. To characterize these  
175 films, UV and <sup>1</sup>H NMR analyses were carried out.

176 To understand the influence of the preparation process on the structure of furfural, UV  
177 analyses were performed on deposited and extracted films in 2 mL of Milli-Q water and  
178 compared to two control solutions of pure furfural solutions at different concentrations (0.01  
179 and 0.02 mM) (Figure 1). The control solutions of furfural presents UV absorption bands at 277  
180 nm and 228 nm, characteristic of the aldehydic and furan functional groups, respectively. We  
181 observed that the UV spectra of films in liquid and solid phases indicated a transformation of  
182 the furfural on the surface with light absorption in the visible range (<600 nm) and presented a  
183 new band at 340 nm. The intense absorption between 200 and 250 nm indicates the conservation  
184 of the furan function while the aldehydic band is shifted, indicating a transformation, which  
185 was later confirmed by  $^1\text{H}$  NMR and PTR-TOF-MS analyses. We hypothesized that the  
186 structure of the film could correspond to polymeric structures, as seen in the literature<sup>44,45</sup>.  
187 Furfural can indeed undergo self-condensation under anhydrous conditions or thermal  
188 treatment at 373–523 K<sup>18,44</sup> and could also form humins<sup>46,47</sup>; however, the mechanism is still  
189 unclear<sup>46–48</sup>. Such chemical processes result in the formation of polyfurylic structures (Figure  
190 2). The band at 340 nm could correspond to maleic anhydride and/or 2-acetylfuran; both of  
191 these are products emitted in the gas-phase from furfural films, as discussed in section 3.2.

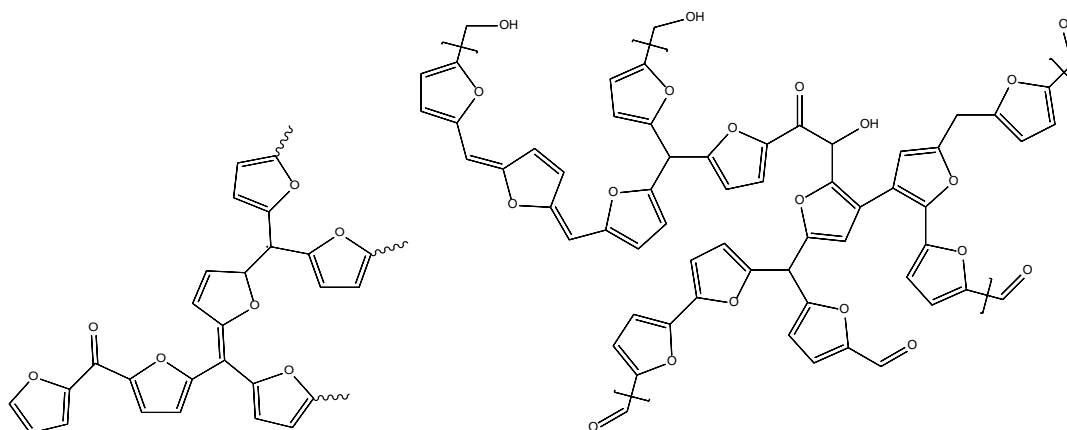
192 The UV analysis of a furfural film that was irradiated by the LED lamp at 340 nm over  
193 time (see Figure S1) showed a change in the shape of the band centered at 340 nm, along the  
194 irradiation time, implying a possible degradation of the sample and a chemical transformation  
195 of the surface. This change in composition upon irradiation will be important for describing the  
196 temporal behavior of HONO emissions discussed in section 3.3.



197

198 **Figure 1:** The UV spectra of a furfural-extracted film, a solid film and aqueous solutions of  
 199 pure furfural (0.01 mM, 0.02 mM). The films were not irradiated.

200



201

202 **Figure 2:** The chemical structure of the suggested polyfurylic oligomer (left)<sup>44</sup> and humins  
 203 (right)<sup>45</sup>

204

205 Moreover, the <sup>1</sup>H NMR analyses showed broad peaks, confirming the complex nature of  
 206 furfural films<sup>49</sup>. The proton peak from the aldehyde (9.4 ppm) group in furfural was not found,  
 207 while the other proton signals could not be identified due to the complexity of the spectra

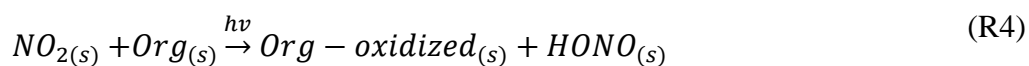
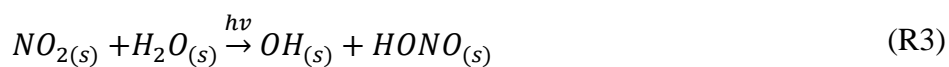
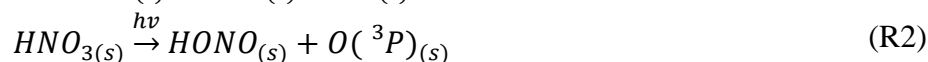
208 between 6 to 8 ppm (see Figure S2a). An important peak at 6.1 ppm was associated with the  
209 presence of an enone group in the structure of the oligomer/humin. The low intensity of the  
210 signal at 9.5 ppm is also in agreement with the hypothesized structure of the oligomer without  
211 aldehydic or carboxylic groups. When potassium nitrate is added to the film, the spectra  
212 changed and new peaks appeared. A peak at 4.9 ppm, absent from samples without potassium  
213 nitrate, indicated the presence of nitro groups (see Figure S2b). The presence of these groups  
214 involved a reaction between nitrate anions and furfural during the film preparation process.  
215 Tests performed on the influence of humidity and irradiation of the film (45 min, with and  
216 without nitrate) did not result in a significant modification of the  $^1\text{H}$  NMR spectra (see SI Figure  
217 2a).

### 218 **3.2. VOC production**

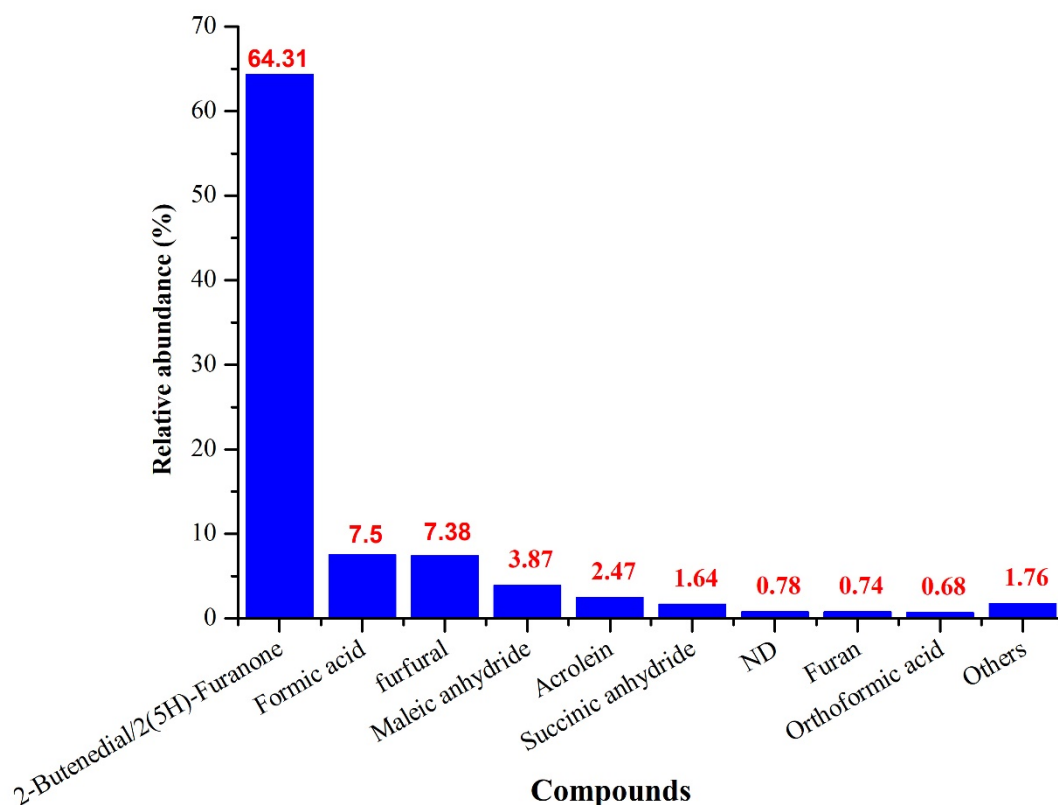
219 The PTR-TOF-MS analyses were performed on furfural films at two different relative  
220 humidities (<1 and 90%) under dark and irradiation conditions without nitrate. When the films  
221 were exposed in the dark to dry synthetic air ( $\text{RH} < 1\%$ ), no significant VOC formation was  
222 observed, however when the humidity was high ( $\text{RH} = 90 \pm 1\%$ ), numerous VOCs were  
223 observed compared to a blank experiment without furfural (see Figure 3 and Table S1). The  
224 presence of the 2,5-Furandicarbaldehyde (also known as 2,5-Diformylfuran; mass-to-charge  
225 ratio of  $m/z = 125.03$ ), 2-Acetylfuran or 5-Methylfurfural ( $m/z = 111.04$ ) and more complex  
226 structures involving derivatives of furan ( $m/z = 123.05$  and  $139.04$ ) confirms the transformation  
227 of furfural during the film preparation, as suggested from the hypothesized oligomeric  
228 structures. Some compounds were unsaturated and possibly conjugated including 2,5-  
229 Diformylfuran, Furylacrolein, 1-(2-Furyl)-1,2-propanedione, explaining the increase of the  
230 maximum of UV absorbance toward visible light, as seen in section 3.1. The presence of  
231 enones, as suggested by the  $^1\text{H}$  NMR analyses, was confirmed by the presence of  
232 malondialdehyde, furylacrolein and acrolein. The compound emitted from the surface with the

233 highest relative abundance had a mass-to-charge ratio of  $m/z = 85.02$ . This ion could be  
 234 attributed to 2(5H)-furanone, which forms from the furfural oxidation under harsher  
 235 conditions<sup>50</sup>. It could also correspond to the isomer 2-butenedial; however, its formation during  
 236 the film preparation is unclear. Under UV irradiation, maleic anhydride ( $m/z = 99.01$ ) was  
 237 formed at high relative abundance (see Figure S3). Photochemistry of both 2(5H)-furanone and  
 238 2-butenedial could explain the formation of maleic anhydride<sup>50-52</sup>. However, only the  
 239 photochemistry of 2-butenedial is activated at the wavelengths used in this study. Experiments  
 240 carried with varying concentrations of oxygen in the gas phase have shown that maleic  
 241 anhydride formation requires the presence of O<sub>2</sub> as described in the mechanism by Newland et  
 242 al.<sup>51</sup> (see Figure S4). Nineteen compounds were found to be released at higher concentrations  
 243 when the sample was irradiated (see Table S2). Direct emissions through the scission of small  
 244 molecules from the suggested structures described in the literature could be the origin of these  
 245 VOCs<sup>53</sup>.

246 The presence of an organic compound (furfural in this study) modifies the molecular structure  
 247 of adsorbed nitrate anions, leading to a red-shift in the actinic region and increasing the light  
 248 absorbed by nitrate anions<sup>54</sup>. Due to the presence of high levels of acids on the surface, nitrate  
 249 is transformed into nitric acid. Adsorbed nitrate/nitric acid (HNO<sub>3(s)</sub>) photolysis can directly  
 250 produce HONO and NO<sub>2</sub> following reactions R1 and R2. It can produce HONO indirectly  
 251 through reactions R3 and R4<sup>54,55</sup>, with Org<sub>(s)</sub> corresponding to furfural in this study, as follows:



252



253

254

255 **Figure 3:** Relative abundance of the most emitted VOCs from furfural films under dark  
 256 condition and at high relative humidity ( $90 \pm 1\%$ )

257

258 The addition of nitrate to the film changed the emission profile of the surface. Concentrations  
 259 of the products emitted from the film with and without irradiation were enhanced up to a factor  
 260 of 10 for maleic anhydride and furfural. Concentrations of compounds of higher mass than the  
 261 furfural were also greatly enhanced; these compounds included succinic/fumaric acid, 2,5-  
 262 Diformylfuran and 1-(2-Furyl)-1,2-propanedione. Unidentified compounds ( $m/z = 151.05$  and  
 263  $169.05$ )  $C_8H_6O_3$  and  $C_8H_8O_4$ , respectively, were also found at higher concentrations. The  
 264 formation of a new compound was also observed at  $m/z = 124.01$  and was identified as  $C_6H_3O_3$ .  
 265 Experiments with different concentrations of nitrate showed an evolution of VOC  
 266 concentrations in relation to the quantity of nitrate on the surface. This increase showed that

267 nitrate interacts with the film and decreases the loss of furfural by evaporation during the sample  
268 preparation.

269

### 270 ***3.3. Addition of nitrate anions – HONO formation***

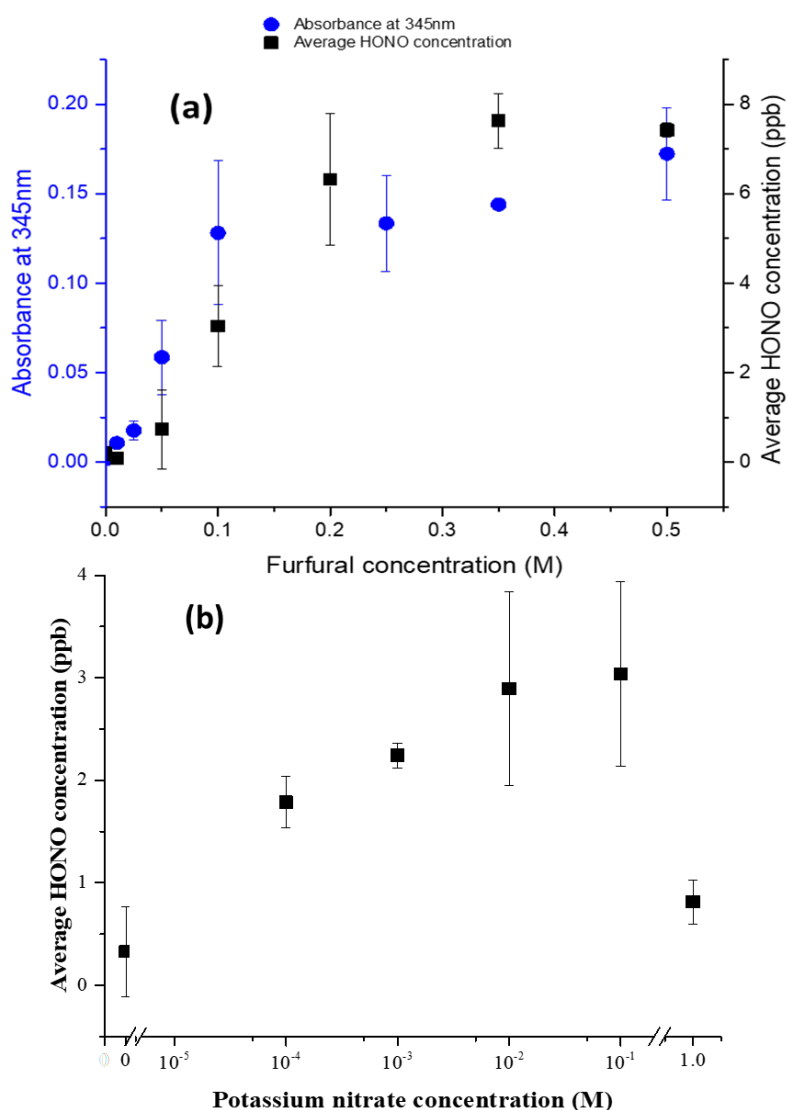
271 Nitrate photochemistry is unlikely to occur under indoor conditions due to the lack of  
272 wavelengths below 330nm. However, a photosensitization pathway could certainly promote its  
273 photo conversion to HONO. In this study we explored this possibility on films made of  
274 deposited furfural

275 When potassium nitrate was added to the furfural films, an enhanced production of HONO  
276 was observed. It is important to underline that under our conditions, in the absence of furfural,  
277 irradiated potassium nitrate on the surface was unable to produce HONO. In fact, the range of  
278 wavelengths (335-380 nm) emitted from the LED lamp used in this experiment does not allow  
279 the activation of the photochemistry of potassium nitrate.  $\text{KNO}_3$  does not absorb significantly  
280 after 335nm<sup>56,57</sup>.

281 The amount of HONO produced was dependent on the quantity of furfural deposited, as  
282 measured by its initial concentration in the parent solution. An increase in the concentration of  
283 furfural from 0.05 to 0.5 M with a concentration of  $10^{-1}$  M of  $\text{KNO}_3$  increased the formation of  
284 HONO by a factor of 10 (Figure 4a). A similar trend can be measured for the absorbance at  
285 345nm of extracted films in water. However, the deposited nitrate mass had only a slight effect  
286 on the formation of HONO from  $10^{-4}$  to  $10^{-1}$  M, which could be expected from a stoichiometric  
287 reaction between the furfural oligomer, the nitrate and a stabilization of the furfural present on  
288 the surface by the nitrate, as the PTR analyses have shown (Figure 4b). Also, when nitrate is  
289 highly concentrated (1 M in the parent solution), the formation of HONO decreases; this is  
290 possibly due to the fact that gaseous products formed in the photolysis process may hardly

291 escape from the nitrate crystal layer formed on the top of the film. This phenomenon was  
292 previously observed by Yang et al <sup>58</sup>. The UV analyses of this film showed a broad absorption  
293 band from 300 to 600 nm, which can prevent the UV irradiation from reaching the furfural film  
294 below the nitrate layer.

295



296

297 **Figure 4:** (a) Formation of nitrous acid from an irradiated film of furfural + KNO<sub>3</sub> (0.1 M) and  
298 the absorbance of the film at 345 nm, as a function of the used furfural concentration. (b)  
299 Formation of nitrous acid from an irradiated film of furfural (0.1 M) + KNO<sub>3</sub> as a function of



300 potassium nitrate concentration. The average HONO concentration was calculated by  
301 integrating the signal during the first 45 minutes of irradiation. Errors are  $\pm 2\sigma$ .

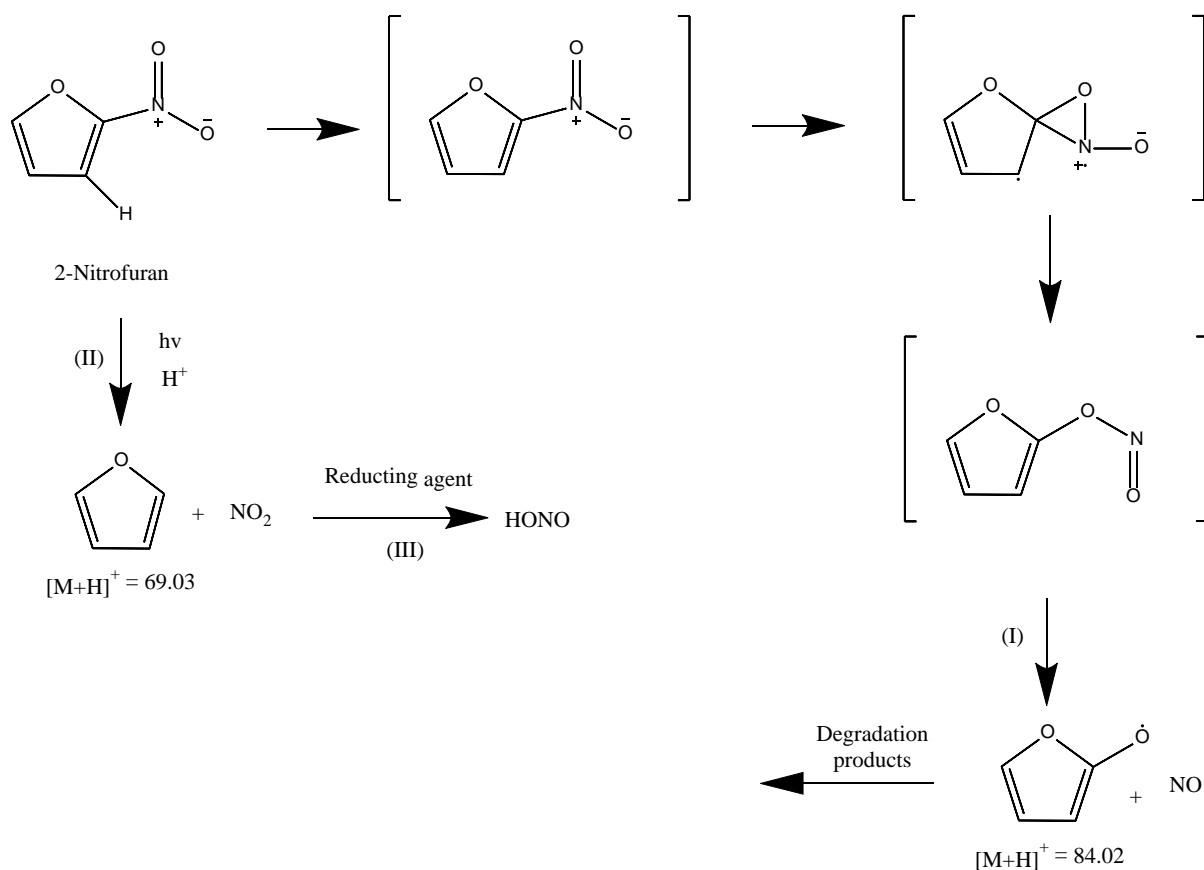
302

303

304 To explain the photochemical formation of NO, NO<sub>2</sub> and HONO, we propose a mechanism  
305 based on our observations and the literature<sup>59-62</sup> (Figure 5). 2-nitrofurans are used as a proxy of  
306 the nitro compounds formed in the film and observed during the NMR analyses. The  
307 degradation of 2-nitrofurans leads to two possible products:  $[M+H]^+ = 84.02$  and  $[M+H]^+ =$   
308  $69.02$  corresponds to C<sub>4</sub>H<sub>3</sub>O<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>O, respectively. Furan is already a product observed  
309 when irradiating a film made from furfural only; however, when nitrate is added, the  
310 photochemistry is enhanced according to the signals detected during the PTR-TOF-MS  
311 analyses. Those products could result from the loss of NO and NO<sub>2</sub> as shown in Figure 5. In  
312 addition, NO<sub>2</sub> could be further reduced to HONO on the surface containing reducing  
313 functionalities such as soot<sup>63</sup> or humic acids<sup>64,65</sup>.

314

315



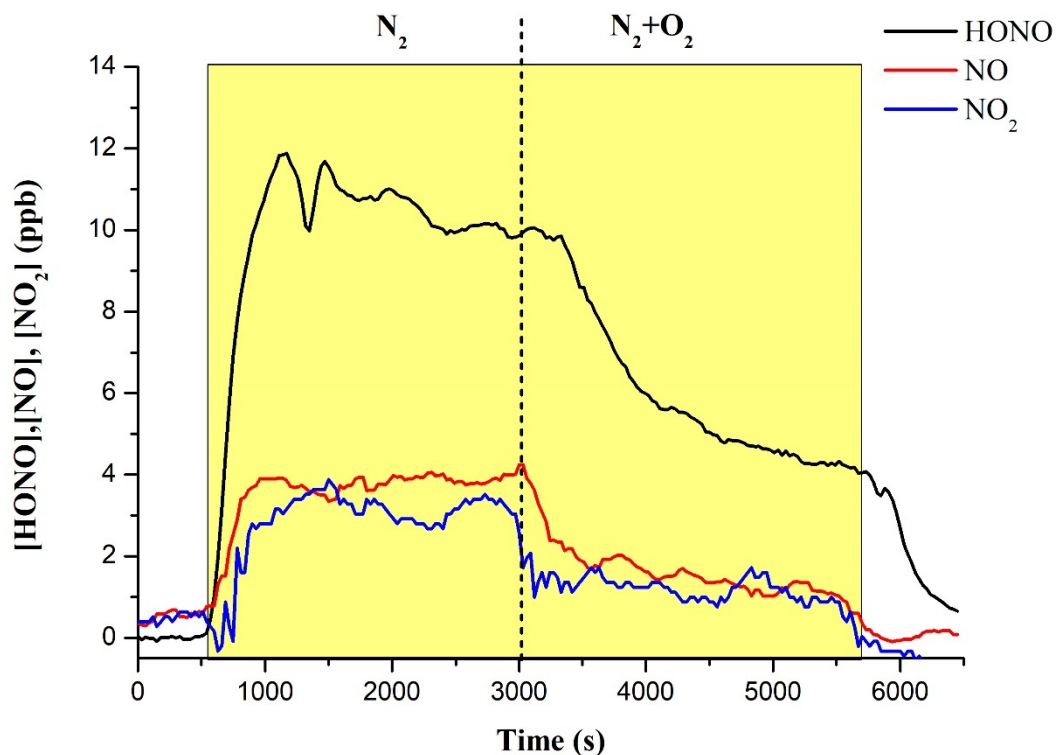
316

317 **Figure 5:** Suggested mechanism of formation of NO, NO<sub>2</sub> and HONO from 2-Nitrofuran under  
 318 UV irradiation.

319

320 This photochemistry was observed under pure nitrogen. The addition of O<sub>2</sub> while maintaining  
 321 a constant flow in the system resulted in decreases of HONO, NO and NO<sub>2</sub> (60%) formation  
 322 rates (Figure 6). The O<sub>2</sub><sup>-</sup> formation at the surface could explain the formation of nitrate, leading  
 323 to losses of nitrogen-containing compounds from the gas phase. O<sub>2</sub><sup>-</sup> production can result from  
 324 the formation of peroxy radicals from the surface which were probed in this study (see next  
 325 section)<sup>66-68</sup>. As O<sub>2</sub><sup>-</sup> is formed, the surface becomes more oxidant, potentially leading to an  
 326 evolution in the mixing ratios of nitrogen containing compounds at the gas-solid interface.

327



328

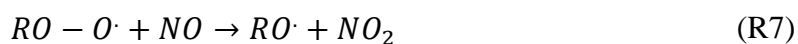
329 **Figure 6:** The formation of HONO, NO and NO<sub>2</sub> from a film of furfural + KNO<sub>3</sub> under UV  
 330 irradiation (yellow section) at RH = 81 ± 2%. The vertical dashed line separates the two  
 331 conditions: N<sub>2</sub> and N<sub>2</sub> + O<sub>2</sub>.

332

### 333 3.4. *NO uptake experiments*

334 A typical result for a NO photo-enhanced uptake experiments on irradiated furfural films is  
 335 presented in Figure 7. The NO was initially chosen as a scavenger of the surface-produced  
 336 peroxy radicals, similar to the study of Hayeck et al<sup>46</sup>. These radicals can react with NO to  
 337 produce NO<sub>2</sub> following reaction (R7):

338

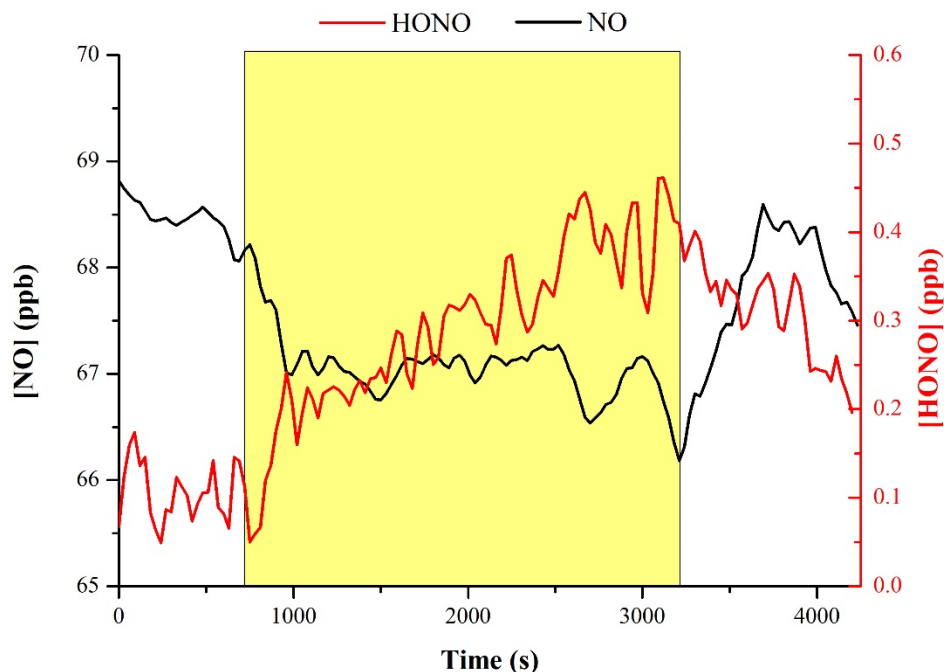


339

340 Tests performed in the absence of O<sub>2</sub> and UV light did not result in any NO uptake due  
341 to the absence of peroxy radicals. Under high relative humidity (RH = 81 ± 2%), furfural films  
342 were unable to uptake NO. This observation could be linked to the presence of a thin layer of  
343 water on the surface of the film, which formed under high relative humidity<sup>39,70</sup>. NO is insoluble  
344 in water<sup>71</sup> so no interaction between the surface and NO was observed. Peroxy radicals could  
345 also be trapped in the liquid phase, preventing their release in the gas phase to react with NO.  
346 However, under indoor-relevant relative humidity (RH = 45 ± 2%), NO is mostly converted  
347 into HONO with a yield lower than 30%. It should be noted that the NO<sub>y</sub>-mass balance is not  
348 closed. That can be explained by the surface formation of nitrogen-containing products.

349 The radical formation from the surfaces could occur due to the presence of furanone / butenedial  
350 under irradiation at  $\lambda \geq 235$  nm, 2(5H)-furanone forms an aldehyde-ketene through a ring-  
351 opening mechanism<sup>50</sup>. Butenedial is able to form radicals under irradiation<sup>51</sup>. Radicals could  
352 also come from the formation of H-abstracted furan and furfural, which were detected in the  
353 PTR-TOF-MS analyses.

354



355

356 **Figure 7:** NO uptake and HONO formation from a furfural film (prepared from 2 mL of 0.5  
 357 M of furfural solution) at  $RH = 45 \pm 2\%$ . Yellow section corresponds to UV irradiation

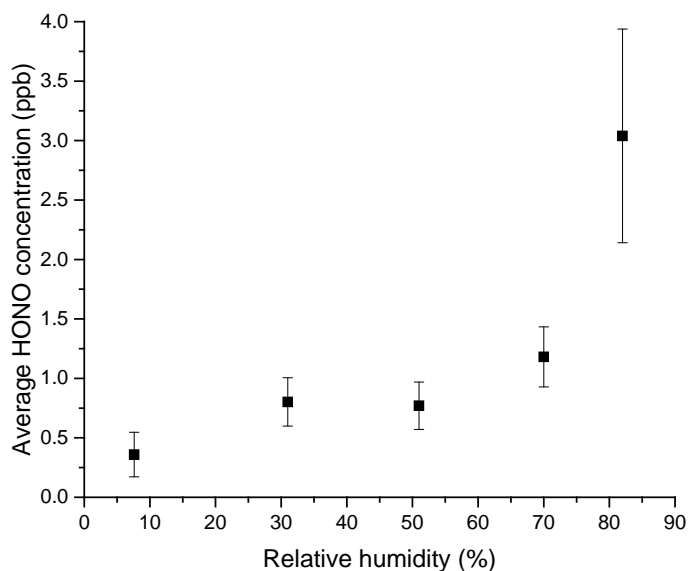
358

### 359 **3.5. Influence of relative humidity**

360 The relative humidity effect on the gas-phase formation of HONO from mixed furfural and  
 361 nitrate anions films is shown in Figure 8. The maximum relative humidity was below the  
 362 deliquescence of potassium nitrate ( $>92\%$ )<sup>73</sup>.

363 During the transition from low to high relative humidity, the HONO formation increased due  
 364 to nitrate photolysis<sup>55</sup>. However, pure potassium nitrate films were unable to produce nitrate.

365 This result could imply that there was a photosensitizer effect from the organic film, which  
 366 enabled nitrate photochemistry at the surface.



367

368 **Figure 8:** The concentration of HONO formed as a function of relative humidity (%) from a  
 369 film prepared with 0.1 M KNO<sub>3</sub> and 0.1 M Furfural. Irradiation time = 45 min.

370

### 371 3.6. HONO source indoor

372 To estimate the concentration of HONO emitted from a surface in a simulated room, HONO  
 373 emission fluxes ( $E_{\text{HONO}}$ ) in  $\mu\text{g m}^{-2} \text{h}^{-1}$  were calculated according to Potard<sup>52</sup>:

$$E_{\text{HONO}} = \frac{F_{\text{air}} \times ([\text{HONO}]_{\text{films}} - [\text{HONO}]_{\text{blank}}) \times M_{\text{HONO}}}{V_{\text{mol}}^{\text{air}} \times S_{\text{exposed}}} \quad (\text{Eq. 1})$$

374

375 where  $F_{\text{air}}$  is the airflow ( $F_{\text{air}} = 0.0054 \text{ m}^3 \text{ h}^{-1}$ ),  $[\text{HONO}]_{\text{films}}$  and  $[\text{HONO}]_{\text{blank}}$  are the  
 376 concentrations of HONO emitted from coated samples and clean glass support (ppb),  
 377 respectively,  $M_{\text{HONO}}$  is the molecular mass of HONO ( $0.047 \text{ kg mol}^{-1}$ ),  $V_{\text{mol}}^{\text{air}}$  is the air molar  
 378 volume at standard temperature and pressure ( $25 \text{ L mol}^{-1}$  at  $25^\circ\text{C}$  and  $1 \text{ atm}$ ) and  $S_{\text{exposed}}$  is the  
 379 exposed surface of nitrate and furfural to light ( $0.002 \text{ m}^2$ ).

380 HONO indoor level depends on the production rate, the surface-area-to-volume ratio of  
 381 the room, the photolysis rate and the ventilation rate. Thus, the indoor concentration of HONO

382 can be determined according to Willem et al.<sup>75</sup>:

$$\frac{d[HONO]}{dt} = \frac{E_{HONO} \times S}{V} - N_h[HONO] - J_{HONO}[HONO] \quad (\text{Eq. 2})$$

383  
384 where  $E_{HONO}$  is the emission rate of HONO in  $\mu\text{g m}^{-2} \text{h}^{-1}$ ,  $S$  is the surface area of the  
385 room ( $\text{m}^2$ ),  $V$  is the room volume ( $\text{m}^3$ ),  $N_h$  is the air exchange rate ( $\text{h}^{-1}$ ) and  $J_{HONO}$  is the  
386 photolysis rate of indoor HONO. Loss on surfaces was not taken into account here as the reactor  
387 used in these experiments present a similar surface-to-volume ratio as the one used in this  
388 simulation. Hence, HONO measured is already impacted by the loss on the surfaces.

389 Assuming there is no influence of outdoor concentration of HONO on the indoor  
390 concentration due to relatively low outdoor levels<sup>76</sup>, the steady-state HONO concentration can  
391 be simplified as:

$$[HONO] = \frac{E_{HONO} \times S}{V \times (J_{HONO} + N_h)} \quad (\text{Eq. 3})$$

392  
393 For indoor-relevant relative humidity ( $\text{RH} = 45\%$ ), with an air exchange rate of  $0.5 \text{ h}^{-1}$   
394 and a photolysis rate of HONO equal to  $0.25 \text{ h}^{-1}$ <sup>31,32</sup> and considering the surface of a room of  
395  $50 \text{ m}^3$  and  $94 \text{ m}^2$  is covered from a film obtained from a solution of  $0.1 \text{ M KNO}_3$  and  $0.1 \text{ M}$   
396 Furfural, HONO concentrations are  $3.9 \text{ ppb}$ .

397 Previous studies were performed on the emission of HONO from the uptake of  $\text{NO}_2$  on  
398 photocatalytic painted surfaces<sup>28,77,78</sup> and with various household surfaces<sup>23</sup>. Conversion yields  
399 up to 90% were observed leading to steady state concentrations of HONO ranging from 1.6 to  
400  $6.3 \text{ ppb}$ . This indicates that furfural film could lead to an increase in HONO production in  
401 presence of  $\text{NO}_2$ .

402 Typical indoor levels of HONO range from 1 to  $10 \text{ ppb}$ <sup>33,79,80</sup>; as such, indoor HONO

403 levels could be significantly affected by surface chemistry as it was previously suggested<sup>11,80</sup>.  
404 HONO can react with indoor pollutants to form carcinogens like nitrosamines<sup>81</sup> and produce  
405 hydroxyl radicals by photolysis. While the direct effect of hydroxyl radicals on health is still  
406 uncertain<sup>82,83</sup>, its role in the formation of toxic compounds like ozone or aerosols indicates a  
407 potential negative effect on indoor air quality.

#### 408 **4. Conclusions**

409 Furfural has been identified as an indoor pollutant<sup>9,15</sup>. Here, we show that this molecule can  
410 react on surfaces, producing complex adsorbed products that initiate photochemistry indoors.  
411 It especially leads to the formation of VOCs and the humidity-dependent formation of nitrous  
412 acid in the presence of co-adsorbed nitrate anions. O<sub>2</sub> can also form peroxy radicals leading to  
413 organic nitrate formation on the surface. As wood-based furniture at home is ubiquitous,  
414 surfaces coated with furfural oligomer are to be expected. Extrapolation of our results to an  
415 indoor environment lead to an estimation of 3.9 ppb at indoor-relevant relative humidity of  
416 45%. HONO reacts with indoor pollutants to form carcinogens compounds as well as producing  
417 OH radicals through photolysis. The presence of indoor OH radicals leads to the formation of  
418 irritating and toxic compounds, altering the indoor air quality.

419

#### 420 **Acknowledgments**

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#### 423 **Data Availability Statement**

424 The data that support the findings of this study are available from the corresponding author  
425 upon reasonable request.

426



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