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# Emissions of the Urban Biocide Terbutryn from Facades: the Contribution of Transformation Products

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1 Emissions of the Urban Biocide Terbutryn from Facades:

2 the Contribution of Transformation Products

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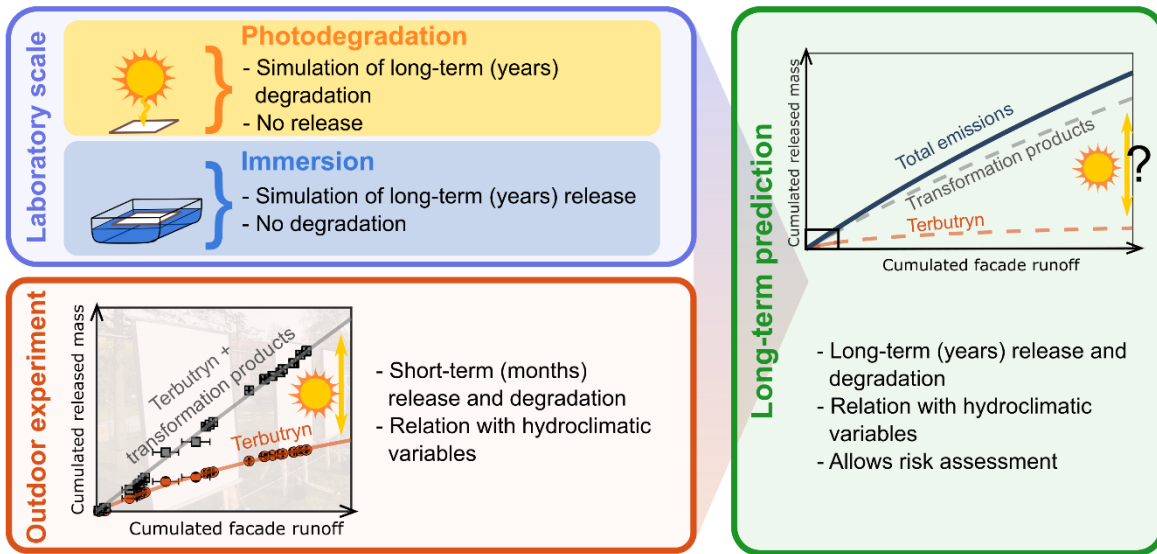
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19 Manuscript for Environmental Science & Technology

20 GRAPHICAL ABSTRACT



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33 ABSTRACT

34 Biocides are added to facade paints and renders to prevent algal and fungal growth.  
35 The emissions of biocides and their transformation products from building facades during  
36 wind-driven rain can contaminate surface waters, soil and groundwater. Although the  
37 emissions of biocide transformation products may be higher than those of the parent biocide,  
38 knowledge of the emissions of transformation products over time is scarce. Combining field  
39 and lab-scale experiments, we showed that solar irradiation on facades controls the formation  
40 of transformation products and can be used with runoff volume to estimate the long-term  
41 emissions of terbutryn transformation products from facades. The slow ( $t_{1/2} > 90$  d)  
42 photodegradation of terbutryn in paint under environmental conditions was associated with  
43 insignificant carbon isotope fractionation ( $\Delta\delta^{13}\text{C} < 2$  ‰) and caused 20 % higher emission of  
44 terbutryn-sulfoxide than terbutryn in leachates from facades. This indicated continuous  
45 terbutryn diffusion toward the paint surface, which favored terbutryn photodegradation and  
46 the concomitant formation of transformation products over time. The emissions of terbutryn  
47 transformation products ( $77 \text{ mg m}^{-2}$ ) in facade leachates, modeled based on irradiation and  
48 facade runoff, were predicted to exceed those of terbutryn ( $42 \text{ mg m}^{-2}$ ) by nearly 2-fold after  
49 eight years. Overall, this study provides a framework to estimate and account for the long-  
50 term emissions of biocide transformation products from building facades to improve the  
51 assessment of environmental risks.

52

53 KEYWORDS: photodegradation, leaching, facade, paint, isotope fractionation, triazine,  
54 compound-specific isotope analysis

55 SYNOPSIS: Knowledge of the emissions of urban biocides and their transformation products  
56 from building facades during wind-driven rain is scarce. This study reports the long-term  
57 emissions of biocides from facades and the relevance of biocide transformation products.

58

## 59 INTRODUCTION

60 Urban biocides added as film preservatives to paints inhibit algae, fungi, and microbial  
61 growth on facades. Biocides can be released into the environment during wind-driven rain.<sup>1,2</sup>  
62 For instance, the triazine biocide terbutryn is used worldwide in construction materials,<sup>3</sup> with  
63 applications of up to 100 t a<sup>-1</sup> in Germany,<sup>4</sup> although it has been banned for agricultural use in  
64 the EU since 2003.<sup>2,5</sup> Terbutryn is toxic to algae, while emissions of several terbutryn  
65 transformation products (TPs), classified as probably toxic, may exceed terbutryn emissions  
66 in facade leachates.<sup>6-8</sup> Biocides are generally entrapped in microcapsules, slowing down their  
67 continuous release from facades.<sup>9-11</sup> Continuous biocide emissions with facade runoff over  
68 years<sup>12,13</sup> may pose ecotoxicological risks in receiving soil, stormwater, surface water, and  
69 potentially the groundwater beneath urban areas.<sup>11-22</sup> In addition, the photodegradation of  
70 biocides on facades may form diverse TPs,<sup>7,16,23</sup> resulting in leaching of biocide-TP mixtures  
71 with unknown ecotoxicological risk.<sup>6</sup> Overall, the processes driving the emissions of biocide  
72 TPs are largely unknown, while approaches to estimate the contribution of TPs to the overall  
73 biocide emissions are currently lacking.

74 A framework combining laboratory and field emission experiments is thus needed to  
75 evaluate the emissions of both biocides and TPs from facades over time. Biocide leaching  
76 from facades involves the dissolution of encapsulated biocides and their diffusion from deeper  
77 layers to the surface, followed by photodegradation and advective transport on the coating  
78 surface.<sup>24</sup> Laboratory immersion tests can simulate long-term biocide emissions.<sup>15,25</sup>  
79 However, their design, i.e., abiotic conditions in the dark, is not appropriate for the

80 quantification of TP emissions throughout the lifespan of facades. This severely limits the use  
81 of laboratory immersion tests to estimate field emissions of biocides and their TPs in long-  
82 term scenarios. For instance, terbutryn emissions have been estimated previously,<sup>7,18,20,24</sup> but  
83 emission models do not account for TPs.<sup>26–28</sup> While field emission experiments under  
84 environmental conditions have often included TP quantification, they are generally conducted  
85 for short periods (e.g., weeks or months), which do not cover the lifespan of facades over  
86 years. As a result, both the short-term emission data from field studies and immersion tests are  
87 currently limited to estimate the long-term emissions of biocides and their TPs.

88 In this context, compound-specific isotope analysis (CSIA) may help to evaluate  
89 terbutryn degradation relying on changes of its stable isotope ratios at naturally occurring  
90 isotopic abundance.<sup>29–33</sup> Indeed, nondegradative processes, such as advection, dilution and  
91 sorption, generally cause insignificant isotope fractionation.<sup>34,35</sup> In a previous study, we  
92 showed that CSIA has the potential to differentiate pathways of terbutryn degradation.<sup>36</sup>  
93 Reaction-specific isotope fractionation values ( $\epsilon$ ) may be used to relate the extent of  
94 degradation to changes in isotope ratios (e.g.,  $\delta^{13}\text{C}$ ).<sup>37–39</sup> However, the potential of CSIA still  
95 needs to be examined to follow up terbutryn degradation in situ, assuming photodegradation  
96 on facades as the main degradation process.

97 We thus hypothesized that irradiation can be used to predict the long-term emissions  
98 of biocides and TPs in leachates from facades and that  $\delta^{13}\text{C}$  measurements can help to  
99 quantify biocide photodegradation in facade paints. Given the worldwide massive use of  
100 terbutryn as a film preservative and the identified gaps of knowledge,<sup>7,18,20,24,36</sup> terbutryn was  
101 used here as a model urban biocide. We examined the degradation and emissions of terbutryn  
102 and its TPs across different temporal scales by combining (i) laboratory photodegradation  
103 experiments with simulated sunlight to evaluate terbutryn degradation and the formation of  
104 TPs in facade paints, (ii) field experiments with artificial facades to assess over months the

105 contribution of TPs in leachates as a function of hydroclimatic variables, and (iii) lab-scale  
106 immersion experiments with facades coated with a paint formulation containing encapsulated  
107 terbutryn to evaluate the long-term (i.e., years) emissions of terbutryn. The overall approach is  
108 summarized in the SI (Scheme S1). Altogether, these experiments allowed the prediction of  
109 terbutryn emissions and the contribution of TPs in leachates from facades to improve risk  
110 assessments. Our results underscored the importance of TPs emissions from building facades,  
111 the role of sunlight irradiation to control the TPs formation and factors controlling the TPs  
112 emissions.

113

## 114 MATERIAL AND METHODS

115 All chemicals used and suppliers are described in the Supporting Information (SI).

### 116 **Terbutryn photodegradation in paint under simulated sunlight**

117 Terbutryn photodegradation experiments were conducted on (i) encapsulated  
118 terbutryn, as currently used commercially in paints; (ii) nonencapsulated terbutryn, as used in  
119 recent decades<sup>40</sup> in facade paint and render; and (iii) paints without terbutryn, from Sto SE &  
120 Co. KGaA (Paint A and B, Table S1) which were spiked with encapsulated terbutryn. Paint A  
121 and B varied in hydrophobicity, binders, and fillers (detailed recipe confidential). Both paints  
122 are commercially available and widely used in Europe. The encapsulated terbutryn  
123 formulation (Troysan CR280, 28 % encapsulated terbutryn) was added to paints at 4 g kg<sup>-1</sup>,  
124 which is the upper range of industrial concentrations and enables terbutryn CSIA. For each  
125 sample, 250 mg of paint (i.e., 278 g paint m<sup>-2</sup> with 1.1 g terbutryn m<sup>-2</sup>) was added to Whatman  
126 glass microfiber filters (Grade GF/F 47 mm diameter). The pure encapsulated and a  
127 nonencapsulated industrial terbutryn formulation (Troysan V662, 48 % terbutryn) were  
128 diluted in ultrapure water (18 mΩ) to 4 g L<sup>-1</sup> terbutryn and spread on filters as 5×50 μL strips  
129 with an automated syringe. All experiments, blanks (paint or empty filters without terbutryn)

130 and dark controls (wrapped in aluminum foil) were dried for one week in the dark.  
131 Photodegradation experiments were carried out in a QSun-XE1 test chamber using a xenon  
132 arc lamp with a Daylight-Q filter with nominal cut-on at 295 nm. The irradiation intensity was  
133  $0.68 \text{ W m}^{-2} \text{ nm}^{-1}$  at 340 nm (i.e., maximum midday solar irradiation), corresponding to an  
134 intensity of  $\approx 1200 \text{ W m}^{-2}$  across wavelengths.<sup>41</sup> Filters were collected over time using a  
135 sacrificial approach (Table S2).

### 136 **Field facade panel leaching experiment**

137 Four  $1 \text{ m}^2$  panels ( $0.65 \text{ m} \times 1.54 \text{ m}$ ) were constructed following the guidelines for  
138 external thermal insulation composite systems (ETICS). Briefly, a polystyrene plate was  
139 glued to a wooden panel protected with a plastic frame and covered with fiberglass  
140 reinforcement mesh within two layers of a biocide-free rendered material (StoSilico blue®  
141 K/MP). Three panels were painted with 350 g of Paint A at  $2.5 \text{ g kg}^{-1}$  of encapsulated  
142 terbutryn, equivalent to  $0.875 \text{ g terbutryn m}^{-2}$ . A fourth panel with Paint A without terbutryn  
143 addition was used as the process blank. To collect facade runoff from each facade, a gutter  
144 coated with Teflon was connected to brown glass bottles and covered under a tarp (Figure  
145 S1). All panels were exposed to the outdoors from April 13th, 2021 (Day 0) to October 24<sup>th</sup>,  
146 2021 (Day 194) in Schiltigheim, district of Adelshoffen, Bas-Rhin, France ( $48^{\circ}36'31.7''\text{N}$ ;  
147  $7^{\circ}44'54.8''\text{E}$ ), facing west, which was the prevailing wind direction. Wind direction,  
148 humidity, temperature, and rainfall data (Table S3) were monitored on site using a Davis  
149 Vantage Vue weather station equipped with a WeatherLink data logger (10 min intervals).  
150 The daily irradiation was obtained from the MeteoFrance station of Entzheim (10 km to the  
151 southwest). In parallel, four panels ( $0.2 \text{ m} \times 0.2 \text{ m}$ ) were prepared similarly for immersion  
152 tests. Those panels were retrieved from the field on Days 0, 33, 160 and 194. Collected  
153 samples for immersion were wrapped in three layers of aluminum foil and frozen at  $-22 \text{ }^{\circ}\text{C}$ .

### 154 **Lab-scale immersion tests for long-term release assessment**



155 Panel pieces (10 cm × 10 cm) were cut from the 1 m<sup>2</sup> panels at the end of the  
156 experiment and from each small facade panel that was collected throughout the study to  
157 account for new facades while considering physical aging through outdoor exposure. The  
158 immersion test followed European standards (EN 16105:2011)<sup>11,42</sup> (SI, page 5). Individual  
159 facade pieces were placed in glass cases and plunged face down in deionized water (100 mL).  
160 The experiment was carried out for 18 days in the dark to prevent photodegradation and  
161 consisted of nine immersion days, including two immersion cycles per immersion day. Nine  
162 immersion days corresponded to a runoff of 10 to 25 years on a facade facing west.<sup>43</sup>

163

#### 164 **Analysis of terbutryn and TPs**

165 Samples from lab-scale photodegradation experiments were extracted using a  
166 modified solid–liquid extraction protocol (detailed in SI).<sup>44,45</sup> Briefly, filters were cut into 0.5  
167 cm<sup>2</sup> pieces and transferred into 40 mL amber glass vials to extract terbutryn using  
168 Pentane:DCM (3:1, V:V).

169 Facade leachate samples were filtered using 0.45 μm PTFE membranes (25 mm Ø,  
170 VWR chemicals). Depending on the concentration, aqueous samples were either directly  
171 injected or extracted using solid phase extraction (SPE) with Chromabond HR-X cartridges  
172 (SI). Terbutryn, and its four major environmentally-relevant TPs<sup>7</sup> terbutryn-sulfoxide  
173 (TerSO), terbutryn-2-hydroxy (TerOH), terbutryn-desethyl (TerDesE) and terbutryn-desethyl-  
174 2-hydroxy (TerDesEOH) were quantified using HPLC–MS/MS (Dionex/Thermo Scientific  
175 UlitMate Dionex 300 coupled to Thermo Scientific TSQ Quantiva) as described previously  
176 (Table S4).<sup>36</sup>

177 Carbon stable isotope analysis was conducted using a GC-IRMS system consisting of  
178 a gas chromatograph (GC, TRACE Ultra ThermoFisher Scientific) coupled to an isotope ratio  
179 mass spectrometer (IRMS, DeltaV plus, ThermoFisher Scientific) via a GC combustion

180 interface (IsoLink/Conflow IV, ThermoFisher Scientific) as described previously.<sup>36</sup> The  
181 terbutryn extraction method did not induce significant carbon isotope fractionation since the  
182 carbon isotope composition of terbutryn from the encapsulated formulation (Troysan CR280)  
183 was the same as that of terbutryn extracted from Paint A and B (Figure S2).

#### 184 **Data analysis**

185 **Predictive emission functions.** The cumulative biocide emissions ( $E_{\log}$ ) in the field  
186 experiments were described with a logarithmic emission function:<sup>46</sup>

$$E_{\log}(q) = a_{char} \cdot \ln\left(1 + 1.72 \frac{q}{q_{char}}\right) \quad (1)$$

187 with  $q$ , the cumulative facade runoff and fitted parameters are the characteristic discharge  $q_{char}$   
188 and the characteristic substance fraction  $a_{char}$ , representing the proportion of the applied  
189 biocide quantity emitted up to the characteristic discharge  $q_{char}$ . Parameters were fitted using  
190 the fit function in MATLAB R2020b.

191 **Correlation between hydroclimatic variables and TPs.** Pearson correlation  
192 coefficients were calculated to examine the relationships between weather data, outdoor  
193 facade leachates of terbutryn, TerSO and TP/terbutryn ratios from collected samples ( $n = 26$ ,  
194 from April 13<sup>th</sup> 2021 (day 0) to October 24<sup>th</sup> (day 194)). The statistical significance level was  
195 set at  $p < 0.05$ . Weather data included rain (mL): cumulative rain since the last sampling event;  
196 temperature: mean temperature ( $^{\circ}\text{C}$ ) since the last sampling event; runoff (mL): collected  
197 facade runoff since the last sampling event; humidity (%): mean humidity since the last  
198 sampling event; dry period (d): time since the last sampling; and irradiation ( $\text{W m}^{-2}$ ):  
199 cumulative irradiation since the last sampling.

200 **Modeling terbutryn and TP emissions from facades.** Terbutryn emissions since the  
201 year of building construction were simulated using COMLEAM.<sup>26</sup> The model calculates  
202 runoff from building components by calculating wind-driven rain from weather data. Biocide  
203 leaching was simulated using emission functions. Rainfall, wind direction and wind speed

204 data were used at a 1 h resolution from 01.01.2014 (building construction) to 31.12.2021 (end  
205 of experiment). Emissions were calculated for the west facade of a standardized building  
206 (OECD house; Table S5, Figure S3 and Figure S4).

207 A scenario was implemented to cover the variability of the solar irradiation intensity  
208 throughout the year. The contribution of TPs to the total biocide emissions (terbutryn + TPs)  
209 was estimated from the ratio of leached TPs to terbutryn (TPs/Ter) as a function of the solar  
210 irradiation and the runoff volume (Eq. 2). The total biocide emissions ( $E_{\text{Ter+TPs}}$ ) were  
211 calculated using facade runoff volumes through wind driven rain based on COMLEAM. Rain  
212 events were defined as days with a rain volume >0.2 mm. The irradiation was calculated as  
213 the sum of the solar irradiation intensities from the end of the previous rain event to the  
214 beginning of the rain event causing biocide emissions. This model used the main drivers of  
215 TP formation and emissions, i.e., irradiation and facade runoff, as predictors for the time  
216 series. The nonlinear relationship was fitted in MATLAB R2021b with the nlinfit function  
217 using the field data for the ratio of TPs/Ter, irradiation since the last rain event (Irr), and  
218 facade runoff volume (q):

$$\frac{TPs}{Ter}(t) = a * \ln(\text{Irr}(t)) + b * e^{c*q(t)} \quad (2)$$

219

## 220 RESULTS

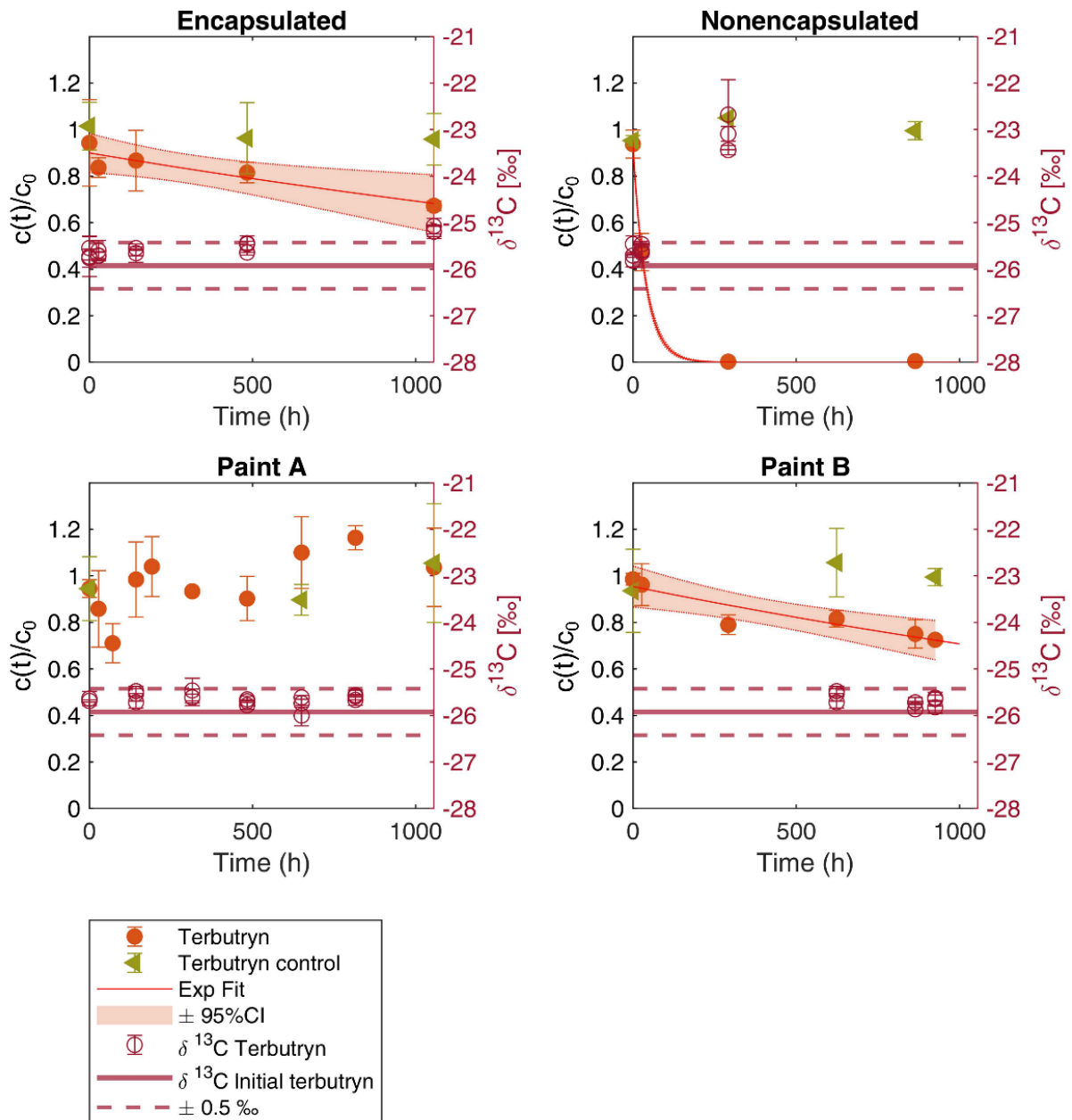
221 **Effect of encapsulation and paint type on terbutryn photodegradation.** Terbutryn  
222 photodegradation prevailed on facades,<sup>7,36,47</sup> although it was limited by both paint and  
223 encapsulation. Less than 30 % of the terbutryn in the pure encapsulated formulation was  
224 degraded after 1000 h ( $t_{1/2}=110 \pm 49$  d) of maximum daily solar irradiation onto a horizontal  
225 surface (Figure 1). This indicates that encapsulation limited terbutryn photodegradation.  
226 Hence, encapsulation slowed the biocide emission from facades and decreased terbutryn  
227 photodegradation in paint, presumably by shielding terbutryn molecules from sunlight. Due to

228 the limited extent of terbutryn degradation and low carbon isotope fractionation values ( $\epsilon_C =$   
229  $-0.7 \pm 0.3$  and  $-0.6 \pm 0.2$  for direct and indirect photodegradation, respectively),<sup>36</sup> the carbon  
230 isotope composition of terbutryn did not change significantly ( $\Delta\delta^{13}C < 1 \text{ ‰}$ ).<sup>36</sup> In contrast, fast  
231 degradation ( $t_{1/2} = 27.5 \pm 1.6 \text{ h}$ ) of terbutryn in the nonencapsulated industrial formulation and  
232 significant stable isotope fractionation ( $\Delta\delta^{13}C = 2.9 \pm 0.4 \text{ ‰}$ ) indicated terbutryn  
233 photodegradation. The extent of degradation (99.7 %) based on the mass balance fitted with  
234 the degradation estimates (99.3 %) based on change in isotope signatures and isotope  
235 fractionation values of terbutryn photodegradation in water.<sup>30,36</sup> This underscores that carbon  
236 CSIA to evaluate the extent of terbutryn photodegradation on facades is limited to an  
237 advanced state of degradation. However, nitrogen ( $\epsilon_N = -1.0 \text{ ‰}$  during indirect  
238 photodegradation in water) or sulfur stable isotopes may result in more pronounced isotopic  
239 fractionation during photodegradation.<sup>36</sup>

240 Terbutryn degradation in Paint A was insignificant while degradation reached 25 % in  
241 Paint B ( $t_{1/2} = 97 \pm 36 \text{ d}$ ) (Figure 1). However, the measurement uncertainty among replicates  
242 and the dark control limited the detection of minor changes ( $< 15 \text{ ‰}$ ) in terbutryn  
243 concentrations. Light penetration was likely restricted to a few  $\mu\text{m}$  of the outer paint layer  
244 (typical facade paint layer thickness  $> 100 \mu\text{m}$ ), thereby limiting terbutryn photodegradation.<sup>24</sup>  
245 Lower terbutryn degradation in pigmented than in pigment-free paints was observed  
246 previously.<sup>23</sup> Faster terbutryn degradation in the pure nonencapsulated than in the  
247 encapsulated formulation indicated that the encapsulation prevents terbutryn from irradiation,  
248 thus decreasing degradation rates. The degradation kinetics of terbutryn on vertical facades  
249 under environmental conditions are expected to be even lower due to diurnal cycles, seasonal  
250 changes in irradiation intensities and facade orientation (i.e., vertical vs. horizontal) compared  
251 to constant irradiation with simulated sunlight at  $> 1000 \text{ W m}^{-2}$ . In addition, different paint  
252 compositions, including pigments and polymers, may favor distinct photodegradation

253 mechanisms.<sup>23</sup> Paint composition can also affect degradation kinetics and pathways of both  
254 biocides and TPs which may result in a different leachate composition.<sup>23,36</sup> For instance, paint  
255 B may favor deeper light penetration or has higher photolytic activity through indirect  
256 photodegradation mechanisms. TPs were not extracted from paint samples because extraction  
257 solvents were selected to isolate terbutryn for CSIA and were not efficient for the extraction  
258 of terbutryn TPs. However, previous studies indicated the formation of TerSO with further  
259 degradation to TerOH or direct degradation to TerOH with further degradation to  
260 TerDesEOH.<sup>23</sup>

261 Carbon isotope fractionation in paints A and B was insignificant ( $\Delta\delta^{13}\text{C} < 1\text{ ‰}$ ),  
262 confirming the moderate extent (<80 %) of terbutryn degradation.<sup>36</sup> In laboratory studies with  
263 fresh paints, the potential of CSIA to follow terbutryn degradation may be limited since a  
264 large fraction of terbutryn is not affected by irradiation. However, in older facades subject to  
265 physical deterioration of the paint and continuous terbutryn diffusion to surface layers of the  
266 paint, CSIA of terbutryn may help evaluate the degradation extent and prevailing pathway on  
267 the facades. Most importantly, the variability of stable isotope ratios of terbutryn in  
268 commercial paint formulations at the source must be small to avoid confounding effects of  
269 isotopically distinct sources when evaluating terbutryn transformation using CSIA. We found  
270 that the terbutryn isotope compositions of eleven commercially available paints were similar  
271 (mean  $\delta^{13}\text{C} = -26.8 \pm 0.8\text{ ‰}$ ; Figure S2). This suggests a homogeneous signature of terbutryn  
272 sources, allowing to evaluate terbutryn transformation in the urban environment using CSIA.



273

274 **Figure 1.** Terbutryn fraction ( $C(t)/C_0$ ) in paints and terbutryn formulations during  
 275 photodegradation under simulated sunlight and for dark controls as a function of time and  
 276 associated change of carbon isotope composition ( $\Delta\delta^{13}C$ ) of terbutryn.

277

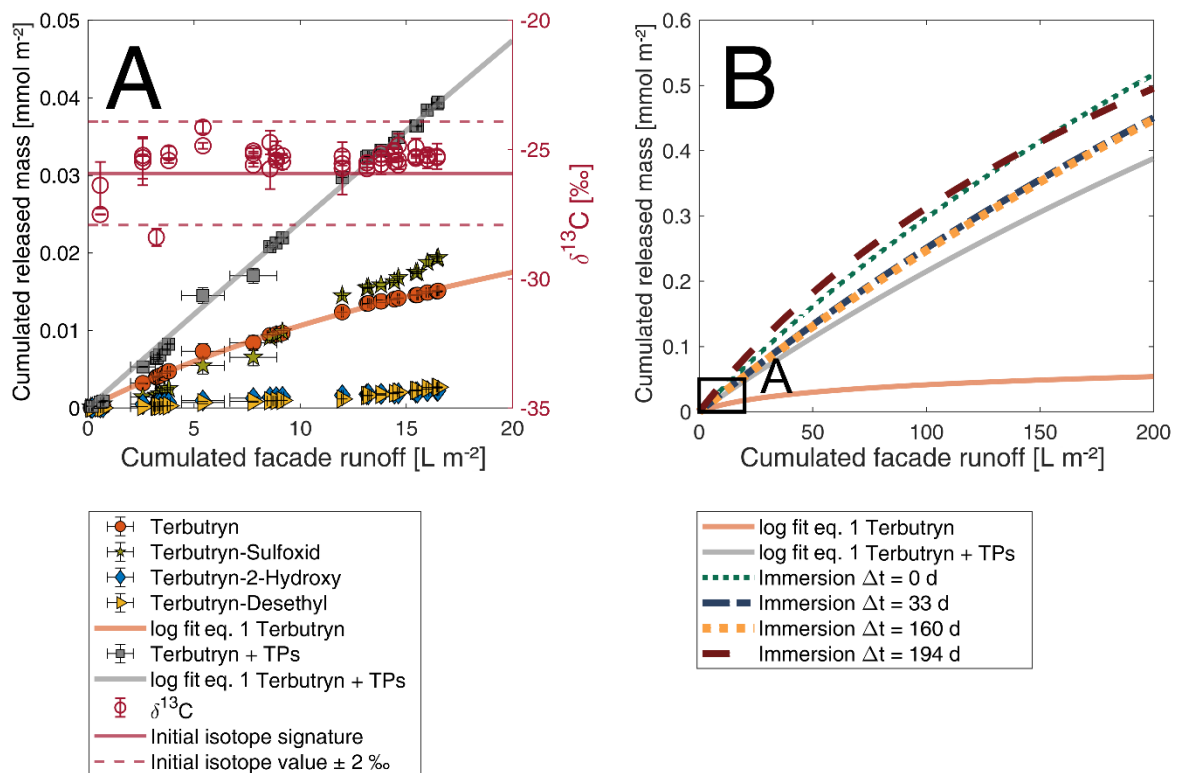
278 **Emissions of terbutryn and transformation products from the field experimental**  
 279 **facades.** The contribution of TPs in facade leachates from the field experimental facades was  
 280 significant (>50 %), which reflected terbutryn photodegradation. Terbutryn emissions from

281 the facades were detected in all leachates, with concentrations ranging from 12 to 387  $\mu\text{g L}^{-1}$ .  
282 Less than 0.02  $\text{mmol m}^{-2}$  terbutryn (i.e., 0.4 % of the initial mass of terbutryn) leached from  
283 the facades within 140 days (Figure 2). When including the terbutryn TPs, the total leached  
284 mass accounted for 1.1 % of the initially applied terbutryn for the same duration. Although  
285 such small leached mass and slow emissions may increase uncertainties for long-term  
286 predictions, continuous photodegradation of terbutryn on the facades led to leaching-driven  
287 release of terbutryn and TPs over time. In contrast, hydrolysis and biodegradation of terbutryn  
288 on facades are expected to be negligible.<sup>14,36</sup> Terbutryn hydrolysis occurs only at extreme pH  
289 values,<sup>36</sup> which do not prevail on facades. While biodegradation and photodegradation can  
290 lead to similar TPs, very slow microbial growth on facade surfaces<sup>48</sup> and limited terbutryn  
291 bioavailability in paint limit biodegradation.

292 TerSO, TerOH and TerDesE were detected in facade leachates, whereas TerDesEOH  
293 could not be detected. The cumulative mass of leached TerSO exceeded that of terbutryn by  
294 20 % after a cumulative facade runoff of 16.5  $\text{L m}^{-2}$  (Figure 2A). This indicates that terbutryn  
295 was initially photodegraded to TerSO. Both direct and indirect photodegradation of terbutryn  
296 may form TerSO as an initial TP. TerSO can sequentially degrade to TerOH and TerDesEOH,  
297 although degradation of TerDesE may also result in TerDesEOH.<sup>7,36</sup> Other TPs, such as  
298 TerOH, may also be formed on facades but might be mobilized to a lesser extent, depending  
299 on the physicochemical properties of the facade and the TPs. For instance, a previous study  
300 with render material showed that more than 20 % of the initial mass of terbutryn was retained  
301 in the facades as TerDesE, TerOH and TerDesEOH after 18 months of exposure.<sup>7</sup>

302 Based on the measured concentrations and emission functions fitted for terbutryn  
303 ( $E_{\text{Ter}}$ ) and the total emissions ( $E_{\text{Ter+TPs}}$ ) of terbutryn and its major TPs, the emissions of  
304  $E_{\text{Ter+TPs}}$  were twice as high as those of  $E_{\text{Ter}}$  across the season (Figure 2A). This underscores  
305 the significant contribution of TPs to the overall biocide emission from facades. This is in

306 agreement with previous observations,<sup>7</sup> and the need to account for TPs in biocide mass  
 307 balances and ecotoxicological risk assessment.<sup>7</sup> The contribution of TPs may be slightly  
 308 underestimated because our study focused on the emissions of four main TPs previously  
 309 identified in facade leachates from render<sup>7</sup>, although the formation of minor TPs cannot be  
 310 excluded. Notably, in contrast to field emission experiments, standard laboratory immersion  
 311 experiments exclude photodegradation and emission functions are typically restricted to the  
 312 parent biocides since immersed facades are not exposed to environmental conditions.<sup>49–51</sup> This  
 313 limits the transferability of results from the laboratory immersion tests to environmental  
 314 conditions. Altogether, our results indicate that irradiation and immersion tests should be  
 315 combined with field experiments to quantify emissions of the parent biocides and their TPs.



316  
 317 **Figure 2.** Mass export of terbutryn and its transformation products (TerSO, TerOH, and  
 318 TerDesE) in leaching from the field experimental facades. A: Emission functions for terbutryn  
 319 (orange) and the sum of terbutryn and TPs (gray) and carbon isotope fractionation of  
 320 terbutryn in facade leachates during 140 days. Error bars for runoff and mass exports indicate



321 standard deviation ( $1\sigma$ ,  $n=3$  facades) and reproducibility for carbon stable isotope analysis  
322 ( $\delta^{13}\text{C}$  of terbutryn,  $n=3$  measurements). B: Logarithmic fit of emission functions for the field  
323 experiments for terbutryn (orange), the sum of terbutryn and TPs from field experiments  
324 (gray) and emissions for the immersion tests of field facades (dotted and dashed lines, by  
325 using freshly painted ( $\Delta t = 0\text{d}$ ) and older facades collected at 33, 160 and 194 d). The  
326 immersion tests correspond to a runoff of 10 to 25 years on a facade facing west. The black  
327 rectangle in the bottom left corner represents the timeframe of the field facade experiment.

328

329 The logarithmic emission function (Eq. 1) fitted the observations of the cumulative  
330 emissions of terbutryn and TPs from facades. Hence, emission rates decreased over time  
331 (Figure 2A),<sup>46</sup> which suggests diffusion-controlled release of terbutryn. The limited terbutryn  
332 photodegradation in paint in the laboratory photodegradation experiments and the high  
333 contribution of TerSO in facade leachates under environmental conditions supports the idea  
334 that photodegradation mainly occurred following terbutryn leaching from the capsules and  
335 diffusive transport toward the paint surface. Hence, terbutryn diffusion to the facade surface is  
336 expected to occur as long as water is in contact with the encapsulation and a concentration  
337 gradient to the facade surface is established. We thus hypothesized that cumulative irradiation  
338 since the last rain event was a key predictor of TP emissions in leachates from facades.

339 Although terbutryn TPs contributed to  $>50\%$  of the released mass in the leachate, the  
340  $\delta^{13}\text{C}$  of terbutryn did not change significantly ( $\Delta\delta^{13}\text{C} < 2\text{‰}$ ) throughout the experiment  
341 (Figure 2A) except for one point, showing an inverse isotope fractionation which cannot be  
342 explained by hydrolysis, photo- or biodegradation.<sup>36</sup> Most  $\delta^{13}\text{C}$  values were similar to the  
343 initial  $\delta^{13}\text{C}$  of terbutryn, although small carbon isotope fractionation could be observed over  
344 time, e.g., after cumulative facade leachate of 5 L, corresponding to a large contribution of

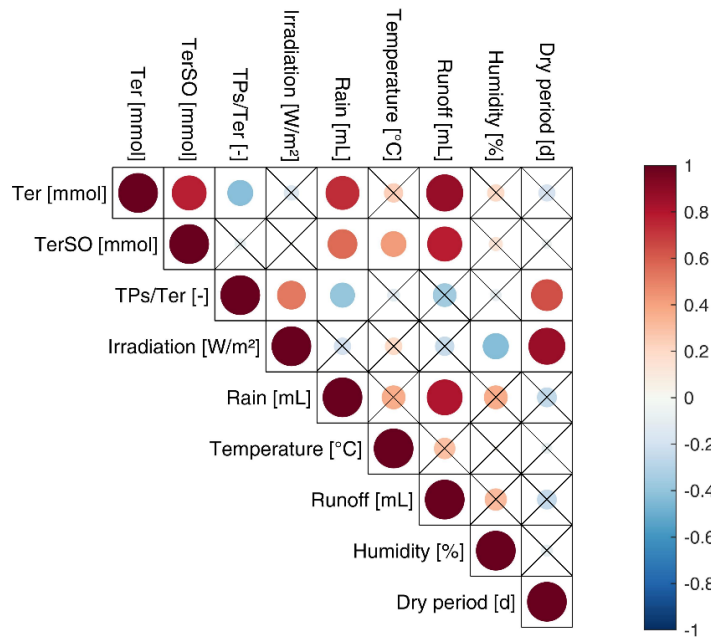
345 TPs. Indeed, the constant diffusion of nondegraded terbutryn bearing its initial isotope  
346 signature from the deeper layer to the facade surface likely diluted the signature of the  
347 remaining pool of terbutryn subject to photodegradation. Such masking of isotope  
348 fractionation by dissolution of contaminants was previously described for non-aqueous phase  
349 liquids in aquifers, especially close to the source zone of contaminants.<sup>52-54</sup> In addition, only a  
350 small carbon isotope fractionation was expected since terbutryn degradation should reach 90  
351 % before significant isotope fractionation (>2‰) can be observed.<sup>55</sup> Significant carbon  
352 isotope fractionation reflecting terbutryn degradation may be, however, theoretically observed  
353 in leachates from small rain events hydrating the outer paint layers after a long period of  
354 terbutryn photodegradation.

355         The limited change of carbon isotopic ratios of terbutryn in leachates of freshly  
356 painted facades limited the applicability of C-CSIA to follow-up degradation on facades.  
357 However, the homogeneous isotopic source signature of terbutryn (i.e., mean  $\delta^{13}\text{C}$  of  
358 terbutryn in paints =  $-26.8 \pm 0.8$  ‰, Figure S2) may allow to follow up terbutryn degradation  
359 using CSIA in compartments receiving facade leachates such as soil and groundwater. Since  
360 CSIA based on carbon alone may not be sufficient to tease apart pathways of terbutryn  
361 transformation, multielement CSIA (ME-CSIA) is needed. Significant nitrogen isotope  
362 fractionation during indirect photodegradation of terbutryn ( $\epsilon = -1.0 \pm 0.4$  ‰) emphasizes the  
363 potential of nitrogen CSIA to follow terbutryn degradation.<sup>36</sup> In addition, sulfur stable isotope  
364 measurements ( $\delta^{34}\text{S}$ ) using GC-MC-ICPMS also hold potential to evaluate terbutryn  
365 degradation and TerSO and TerOH formation,<sup>56</sup> since the bond formation between the sulfur  
366 and oxygen atoms may cause a significant inverse isotope effect (i.e., a depletion in  $^{34}\text{S}$  in the  
367 non-degraded terbutryn fraction).

368

369           **Factors controlling transformation and emissions of terbutryn and TPs from**  
370 **facades.** The cumulative irradiation intensity mainly controlled the contribution of TPs to the  
371 overall terbutryn emissions from facades. Both terbutryn and TerSO emissions in leachates  
372 significantly correlated with the runoff amount ( $p < 0.005$ , Figure 3, S5 and S6). It is expected  
373 that longer and more intense rain events generate a continuous diffusion gradient of biocide  
374 and TP concentrations from the inner to the outer paint layers, resulting in rainfall-  
375 proportional emissions.

376           The ratio of leached TPs to terbutryn (TPs/terbutryn) correlated positively ( $p < 0.05$ )  
377 with the cumulative irradiation intensities and time since the last rainfall and negatively  
378 ( $p < 0.1$ ) with rainfall and runoff volumes. This confirms that solar radiation is the main driver  
379 of photodegradation and can be used as a predictor of TPs emissions from facades. This also  
380 indicates that TPs are formed predominantly during spells with high irradiation and low  
381 rainfall, before being leached from the outer paint layer during strong and long-lasting rain  
382 events. In contrast, terbutryn was continuously mobilized from the facade and mainly  
383 contributed to biocide emissions over time. This supports the idea that the contribution of TPs  
384 is limited to the photodegraded terbutryn fraction on the paint surface, whereas the large pool  
385 of terbutryn diffuse continuously during long rain events. Heavy and long rain events may  
386 also increase the residual water content in the facade after rain events. This may, in turn,  
387 increase the terbutryn diffusion and the renewal of the photodegradable fraction of terbutryn  
388 in the paint surface. Regarding the contribution of different TPs to the overall biocide  
389 leaching, TerOH and TerDesE may diffuse at a slower rate than TerSO and thus contribute  
390 less to the total emission.<sup>7</sup>



391

392 **Figure 3.** Pearson correlation coefficients between event-based emissions of terbutryn (Ter)  
 393 and terbutryn-sulfoxide (TerSO), the ratio of all TPs to terbutryn (TPs/Ter) and hydroclimatic  
 394 variables. Crossed out cells indicate nonsignificant correlations ( $p > 0.05$ ). The size of the  
 395 circle indicates the value of the correlation coefficient. Positive correlations are displayed in  
 396 red and negative correlations in blue color.

397

398 **Predicting leaching of terbutryn and TPs from facades.** The difference between the  
 399 logarithmic fit of emission functions (Eq. 1) for terbutryn and for terbutryn + TPs (Figure 1,  
 400 Table S6) indicates that considering terbutryn without TPs leads to an underestimation of  
 401 biocide leaching by  $>50\%$  after 194 days. Extrapolating the emission functions increased the  
 402 contribution of TPs over time (Figure 2B), since experiments were conducted in spring and  
 403 summer under higher solar irradiation intensities than in winter. When considering TPs, the  
 404 biocide emissions from the field facades and from the immersion tests were similar for the  
 405 same volume of simulated runoff (Figure 2B). This supports the assumption that the amount  
 406 of water in contact with the facade controls the total biocide emissions, and that diffusion-

407 controlled leaching of biocides is accounted for in laboratory immersion tests. Older facades  
408 retrieved from the field experiment after  $\Delta t = 33$  d, 160 d and 194 d had similar leaching  
409 patterns to those of freshly painted facades (Figure 2B, Table S6). This suggests that physical  
410 deterioration of the facades during a few months had only a minor impact on biocide  
411 emissions.

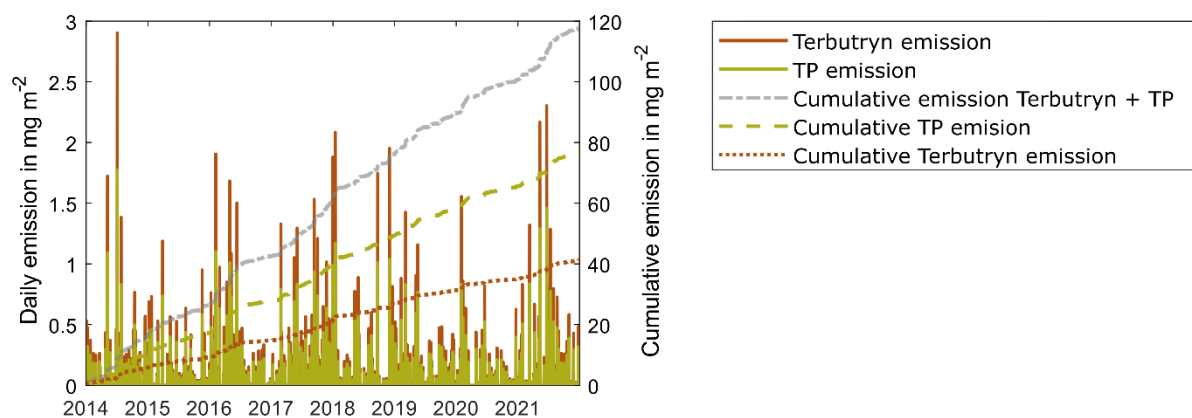
412 A comparison of emissions from immersion tests with extrapolated emissions from  
413 field experiments indicated that emissions of Ter + TPs were underestimated by <25 %. This  
414 may be due to the minor contribution of TPs in leachates (i.e., terbutryn-desbutyl-2-hydroxy,  
415 terbutryn-desbutyl, terbutryn-desthiomethyl-desbutyl, and terbutryn-desthiomethyl-desethyl)  
416 that were not targeted in our study.<sup>6,7,47</sup> The cumulative facade runoff ( $q$ ) to release a specific  
417 amount of biocides can be estimated from Eq. 1, considering terbutryn only or both terbutryn  
418 and TPs. The results indicate that biocide emissions were largely underestimated when TPs  
419 were not accounted for (Table S6).

420 Although the terbutryn emission in leachate decreases over time, different TPs may  
421 accumulate in the facade material and increasingly contribute to emissions of biocide  
422 residues.<sup>8</sup> Even though no degradation during the immersion tests was expected, TerOH was  
423 continuously released with a minor contribution of TerSO, especially from panels previously  
424 exposed to field conditions (e.g., for 160 d and 194 d, Figure S7). Additionally, TerDesEOH  
425 and TerDesE were released in the immersion experiment (Figure S7). This confirmed that  
426 some TPs formed over time under environmental exposition but were likely retained in the  
427 facade material and mobilized only with a large amount of water. This is also in line with  
428 previous field experiments with render as an external coating. Previous experiments showed  
429 that TerOH and other TPs, such as TerDesE, can be retained in the facade, leading to small  
430 but continuous release.<sup>7</sup> Additionally, elution experiments with 1 L water per 0.25 m<sup>2</sup> on 13-  
431 year-old facades indicated a release of TerOH that was one order of magnitude higher than

432 that of terbutryn. In contrast, grab samples after natural rain events showed higher terbutryn  
433 concentrations.<sup>13</sup> This indicated retention of TerOH in the facade, with emissions following  
434 long periods with heavy rain events.

435 The implementation of biocide emission curves into the COMLEAM model allowed  
436 to estimate the contribution of TPs to the overall biocide emissions over time, for instance  
437 eight years from the building construction. For the initial conditions (e.g.,  $C_{0 \text{ Terbutryn}}=1416 \text{ mg}$   
438  $\text{m}^{-2}$ ), the emission functions for the total emissions ( $E_{\text{Ter+TPs}}$ ) underscored the release of 8.4 %  
439 ( $118 \text{ mg m}^{-2}$ ) of the initial applied mass (Figure 4).

440 A TPs to Ter ratio of 3:2 indicated a significant contribution of TPs over time,  
441 accounting for both summer and winter irradiation conditions in the model. The fitted values  
442 for Eq. 2 were  $a = 0.164$ ,  $b = 1.422$  and  $c = -0.858$ , yielding a good fit ( $R^2=0.97$ ) between the  
443 measured and simulated ratios of TPs/Ter (Figure S8). The simulated emissions of TPs ( $77$   
444  $\text{mg m}^{-2}$ ) were higher than those of terbutryn ( $42 \text{ mg m}^{-2}$ ) over 8 years (Figure 4). Although  
445 other parameters may influence the contribution of TPs in leachate, irradiation and facade  
446 runoff were sufficient predictors of biocide and TP leaching from facades. The simulated  
447 TPs/Ter ratios are in agreement with grab samples close to facades in old districts ( $>10$   
448 years).<sup>12,13</sup> In the latter studies, ratios of TP/Ter varied between samplings. This suggests an  
449 effect of hydroclimatic variables, although records on preceded whether conditions were  
450 lacking. While TPs concentrations exceeded Ter nearly 10-fold in single samples, most  
451 concentrations of Ter and TPs were similar. Hence, the approach proposed in the present  
452 study may be used to implement release models of mixtures of TPs and parent biocides to  
453 predict emissions and potential ecotoxicological risks in compartments receiving leachates  
454 from facades.



455  
 456 **Figure 4.** Modelling results of total emissions of terbutryn and TPs and cumulative emissions  
 457 per m<sup>2</sup> of facade from 2014 to 2021, based on runoff and irradiation correlation for the  
 458 contribution of TPs in leachate.

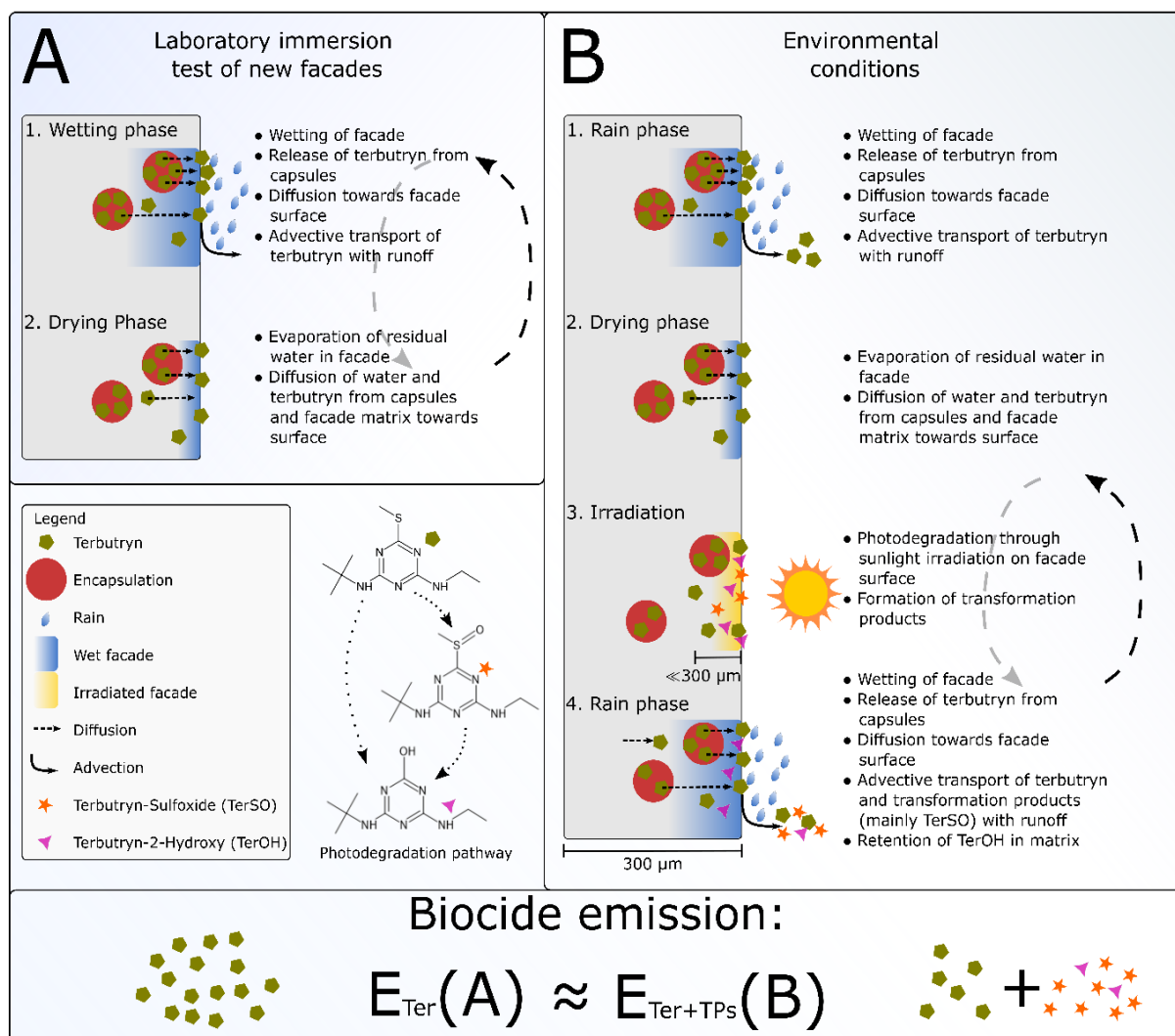
459  
 460 **Environmental implications for the estimation of biocide leaching from facades.**

461 Previous studies underscored the significant leaching of terbutryn TPs from facades.<sup>7,12,13,57</sup>  
 462 However, key drivers controlling TP leaching have not yet been identified, and the  
 463 contribution of TPs to the overall biocide leaching has not been quantified. Thus, by  
 464 combining field experiments with laboratory immersion tests, the influence and contribution  
 465 of hydroclimatic variables on TP emissions was determined. Our results confirmed that  
 466 photodegradation is the key process responsible for terbutryn degradation in the facades. This  
 467 supports the idea that degradation occurs predominantly after terbutryn diffusion from  
 468 microcapsules toward the outer paint layer (Figure 5), as also indicated by CSIA data. Even  
 469 though no significant changes of carbon isotope composition (<2 ‰) of terbutryn was  
 470 observed in the field experiments, this study paves the way for broader application of CSIA to  
 471 various urban organic contaminants. In particular, the absence of isotope fractionation for  
 472 terbutryn in facade leachates may help to evaluate terbutryn degradation in environmental

473 compartments receiving biocide leachates and runoffs, assuming a homogeneous source  
474 isotope signature in terbutryn in the facades.

475 Climate change may have little impact on terbutryn leaching from facades. However,  
476 increased temperatures by 1.5 to 4.5 °C over the next 100 years<sup>58</sup> may accelerate diffusion-  
477 controlled emissions. Rainfall patterns can also affect emitted mass, with strong rainfall  
478 events mobilizing more terbutryn, and droughts and concomitant solar irradiation periods  
479 increasing TP contribution. To further consolidate and generalize our results, field  
480 experiments should be conducted with various paint and render systems since they might  
481 result in different degradation rates of Ter and contributions of TPs (Figure 1).





483

484 **Figure 5.** Proposed leaching sequence of terbutryn (Ter) and TPs (TerSO and TerOH) from  
 485 facades in four steps (adapted from Uhlig et al., 2019<sup>24</sup>). Under environmental conditions,  
 486 Steps 2 and 3 might occur simultaneously.

487

488 Overall, our study supports the sequence of terbutryn emission-degradation suggested  
 489 previously,<sup>24</sup> and proposes a framework to assess biocide and TP emissions from facades to  
 490 improve risk assessment for the sustainable use of urban runoff. Under field conditions,

491 diffusion is a major process of terbutryn release, which is accompanied by photodegradation  
492 during the drying phase of the facades (Figure 5).

493 Because the emission rates of terbutryn and TPs are mainly dependent on terbutryn  
494 diffusion, emissions ( $E_{\text{Ter}}(\text{A})$ ) in immersion tests are similar to those of terbutryn and TPs  
495 ( $E_{\text{Ter+TPs}}(\text{B})$ ) in the field emission experiments. Thus, immersion tests can be used to evaluate  
496 long-term biocide emissions, but accounting for TP formation is required to deliver realistic  
497 environmental emission scenarios (Figure 5).

498 Most importantly, solar irradiation and facade runoff are the main predictors to  
499 estimate the contribution of TPs to the overall biocide leaching and to estimate the emission  
500 of TPs over long time periods. Our results showed that >60 % of terbutryn can be emitted  
501 from the facades as TPs over long time periods (i.e., 8 years). Disregarding the emissions of  
502 biocide TPs can leads to a severe underestimation of both biocide leaching and associated  
503 toxicological risks in receiving compartments. Therefore, we anticipate our results to be a  
504 starting point to integrate TPs for a more accurate and robust evaluation and prediction of the  
505 environmental impacts of biocide leaching from facade paints.

506

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#### 517 SUPPORTING INFORMATION AVAILABLE

518 The Supporting Information is available free of charge at XXXX.

#### 519 AUTHOR CONTRIBUTION STATEMENT

520 **Tobias Junginger:** Conceptualization; Data curation; Formal analysis; Investigation;  
521 Methodology; Visualization; Writing – original draft. **Sylvain Payraudeau:** Formal analysis;  
522 Resources; Software; Supervision; Validation; Writing – review & editing. **Gwenaël Imfeld:**  
523 Conceptualization; Data curation; Formal analysis; Funding acquisition; Methodology;  
524 Project administration; Resources; Supervision; Validation; Visualization; Writing – review &  
525 editing.

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