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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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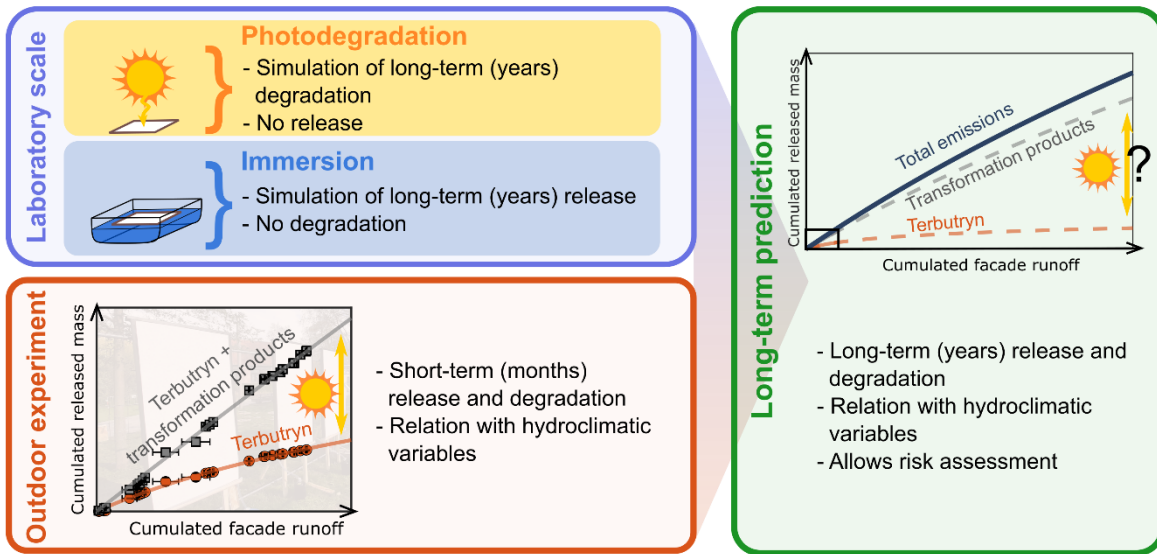
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19 Manuscript for Environmental Science & Technology

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 mg m^{-2}) in facade leachates, modeled based on irradiation and
48 facade runoff, were predicted to exceed those of terbutryn (42 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.^{1,2}
62 For instance, the triazine biocide terbutryn is used worldwide in construction materials,³ with
63 applications of up to 100 t a⁻¹ in Germany,⁴ although it has been banned for agricultural use in
64 the EU since 2003.^{2,5} 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.⁶⁻⁸ Biocides are generally entrapped in microcapsules, slowing down their
67 continuous release from facades.⁹⁻¹¹ Continuous biocide emissions with facade runoff over
68 years^{12,13} may pose ecotoxicological risks in receiving soil, stormwater, surface water, and
69 potentially the groundwater beneath urban areas.¹¹⁻²² In addition, the photodegradation of
70 biocides on facades may form diverse TPs,^{7,16,23} resulting in leaching of biocide-TP mixtures
71 with unknown ecotoxicological risk.⁶ 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.²⁴ Laboratory immersion tests can simulate long-term biocide emissions.^{15,25}
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,^{7,18,20,24} but
83 emission models do not account for TPs.^{26–28} 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.^{29–33} Indeed, nondegradative processes, such as advection, dilution and
91 sorption, generally cause insignificant isotope fractionation.^{34,35} In a previous study, we
92 showed that CSIA has the potential to differentiate pathways of terbutryn degradation.³⁶
93 Reaction-specific isotope fractionation values (ϵ) may be used to relate the extent of
94 degradation to changes in isotope ratios (e.g., $\delta^{13}\text{C}$).^{37–39} 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,^{7,18,20,24,36} 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 decades⁴⁰ 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⁻¹,
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⁻² with 1.1 g terbutryn m⁻²) 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⁻¹ 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.⁴¹ Filters were collected over time using a
135 sacrificial approach (Table S2).

136 **Field facade panel leaching experiment**

137 Four 1 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 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 24th,
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 m² 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)^{11,42} (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.⁴³

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).^{44,45} Briefly, filters were cut into 0.5
167 cm² 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 TPs⁷ 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).³⁶

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.³⁶ 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:⁴⁶

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

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 13th 2021 (day 0) to October 24th (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 (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.²⁶ 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):

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

219

220 RESULTS

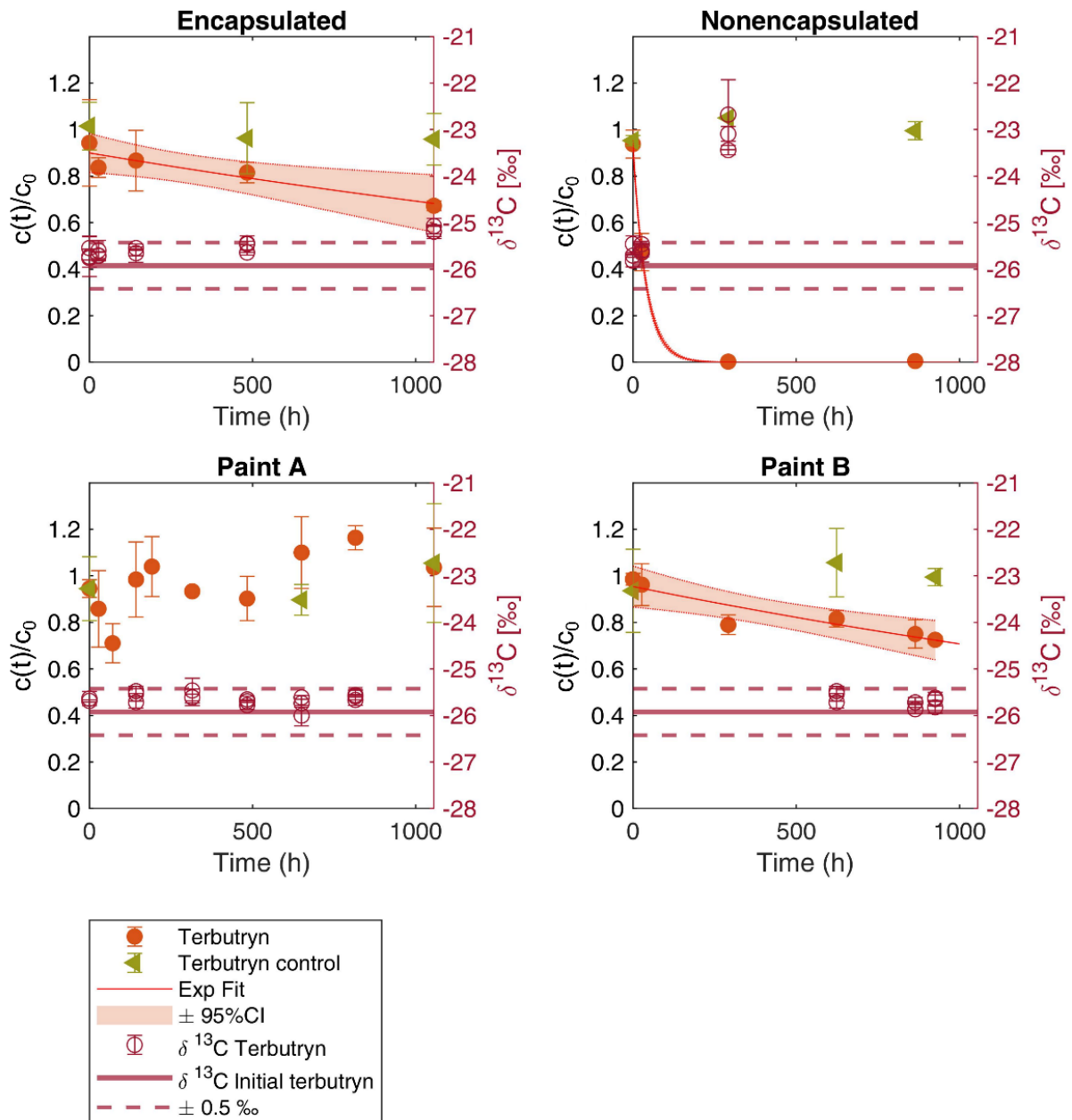
221 **Effect of encapsulation and paint type on terbutryn photodegradation.** Terbutryn
222 photodegradation prevailed on facades,^{7,36,47} although it was limited by both paint and
223 encapsulation. Less than 30 % of the terbutryn in the pure encapsulated formulation was
224 degraded after 1000 h ($t_{1/2}=110 \pm 49$ 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 ± 0.3 and -0.6 ± 0.2 for direct and indirect photodegradation, respectively),³⁶ the carbon
230 isotope composition of terbutryn did not change significantly ($\Delta\delta^{13}C < 1 \text{ ‰}$).³⁶ 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.^{30,36} 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.³⁶

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 μm of the outer paint layer
244 (typical facade paint layer thickness $> 100 \mu\text{m}$), thereby limiting terbutryn photodegradation.²⁴
245 Lower terbutryn degradation in pigmented than in pigment-free paints was observed
246 previously.²³ 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.²³ Paint composition can also affect degradation kinetics and pathways of both
254 biocides and TPs which may result in a different leachate composition.^{23,36} 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.²³

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.³⁶ 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

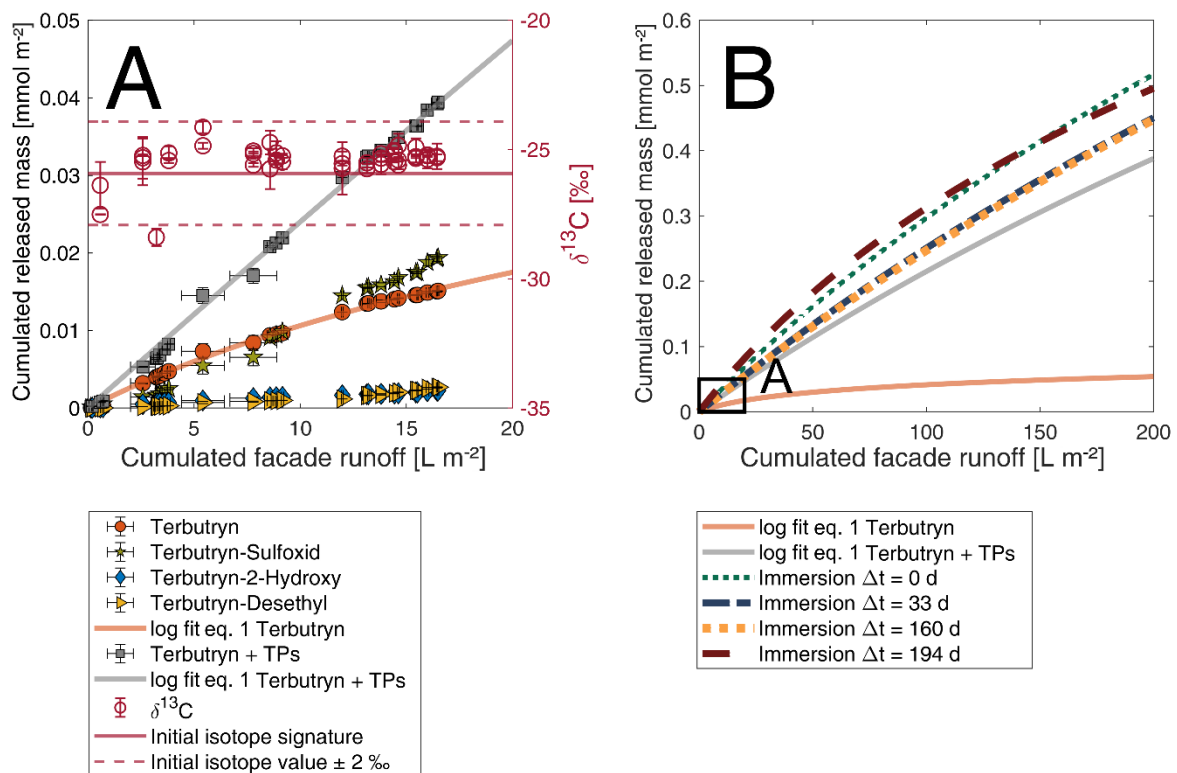
278 **Emissions of terbutryn and transformation products from the field experimental**
 279 **facades.** The contribution of TPs in facade leachates from the field experimental facades was
 280 significant (>50 %), which reflected terbutryn photodegradation. Terbutryn emissions from

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 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.^{14,36} Terbutryn hydrolysis occurs only at extreme pH
289 values,³⁶ which do not prevail on facades. While biodegradation and photodegradation can
290 lead to similar TPs, very slow microbial growth on facade surfaces⁴⁸ 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 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.^{7,36} 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.⁷

302 Based on the measured concentrations and emission functions fitted for terbutryn
303 (E_{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_{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,⁷ and the need to account for TPs in biocide mass
 307 balances and ecotoxicological risk assessment.⁷ 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 render⁷, 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.^{49–51} 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 (1σ , $n=3$ 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),⁴⁶ 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.³⁶ 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

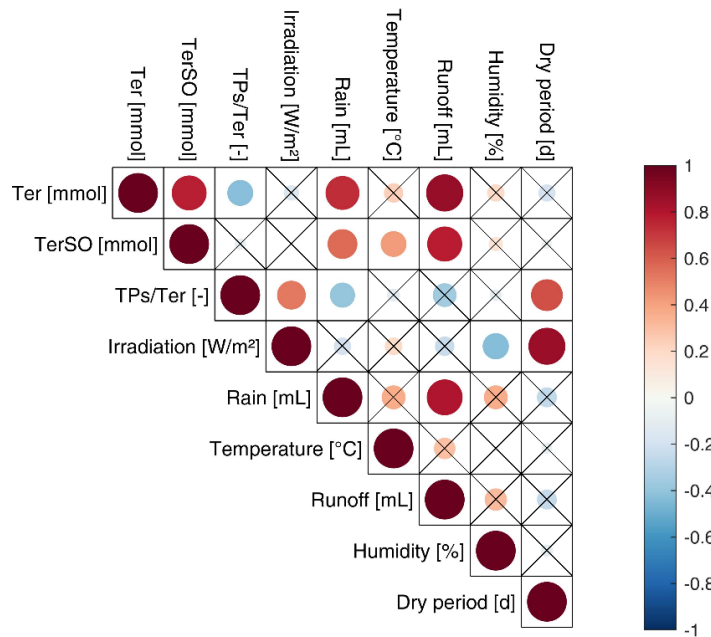
345 TPs. Indeed, the constant diffusion of nondegraded terbutryn bearing its initial isotope
346 signature from the deeper layer to the facade surface likely diluted the signature of the
347 remaining pool of terbutryn subject to photodegradation. Such masking of isotope
348 fractionation by dissolution of contaminants was previously described for non-aqueous phase
349 liquids in aquifers, especially close to the source zone of contaminants.⁵²⁻⁵⁴ 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.⁵⁵ 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 ± 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.³⁶ 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,⁵⁶ since the bond formation between the sulfur
366 and oxygen atoms may cause a significant inverse isotope effect (i.e., a depletion in ^{34}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.⁷



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.

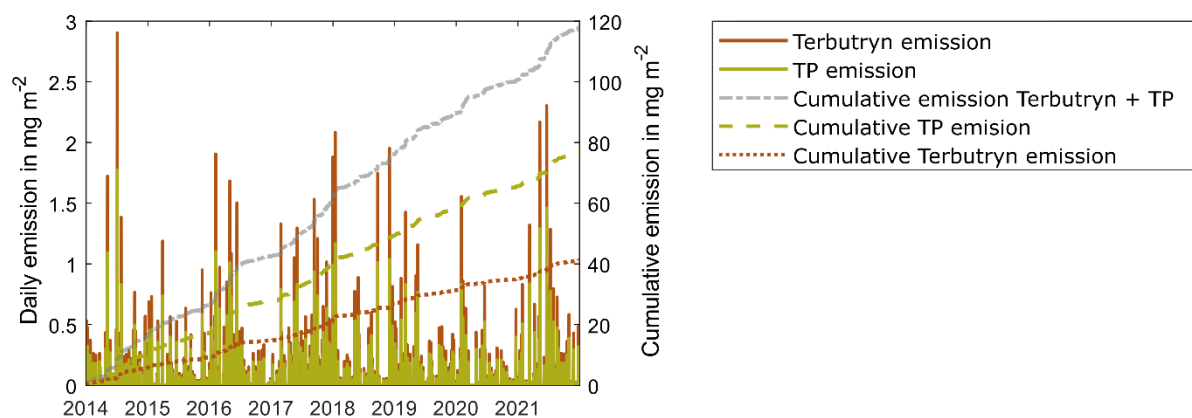
412 A comparison of emissions from immersion tests with extrapolated emissions from
413 field experiments indicated that emissions of Ter + TPs were underestimated by <25 %. This
414 may be due to the minor contribution of TPs in leachates (i.e., terbutryn-desbutyl-2-hydroxy,
415 terbutryn-desbutyl, terbutryn-desthiomethyl-desbutyl, and terbutryn-desthiomethyl-desethyl)
416 that were not targeted in our study.^{6,7,47} 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.⁸ 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.⁷ Additionally, elution experiments with 1 L water per 0.25 m² 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.¹³ 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 m^{-2}), the emission functions for the total emissions ($E_{\text{Ter+TPs}}$) underscored the release of 8.4 %
439 (118 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 mg m^{-2}) were higher than those of terbutryn (42 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).^{12,13} 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.



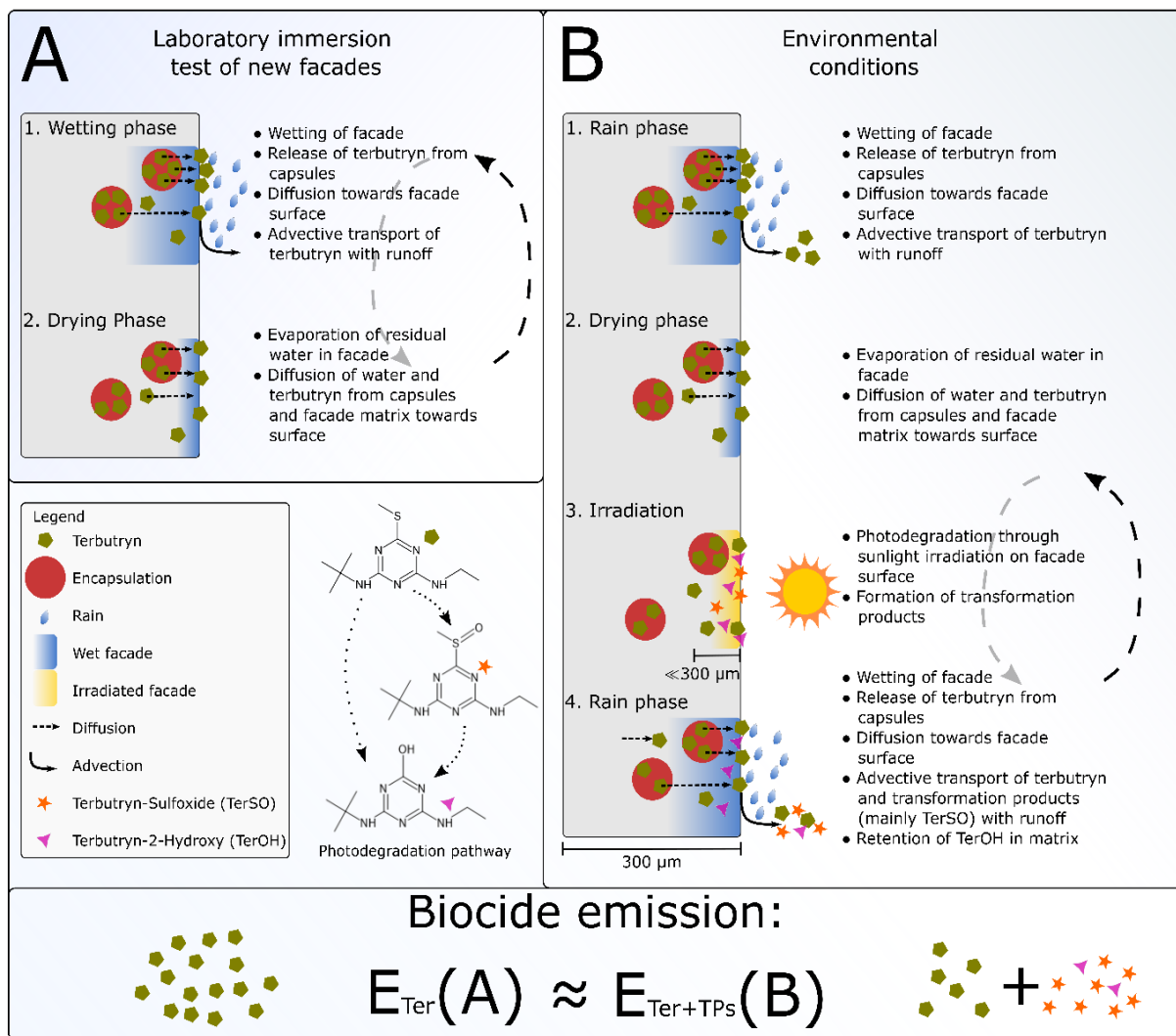
455
 456 **Figure 4.** Modelling results of total emissions of terbutryn and TPs and cumulative emissions
 457 per m² of facade from 2014 to 2021, based on runoff and irradiation correlation for the
 458 contribution of TPs in leachate.

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

461 Previous studies underscored the significant leaching of terbutryn TPs from facades.^{7,12,13,57}
 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 years⁵⁸ 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., 2019²⁴). 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,²⁴ 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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