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1 **Transformation and stable isotope fractionation of the urban biocide terbutryn**
2 **during biodegradation, photodegradation and abiotic hydrolysis**

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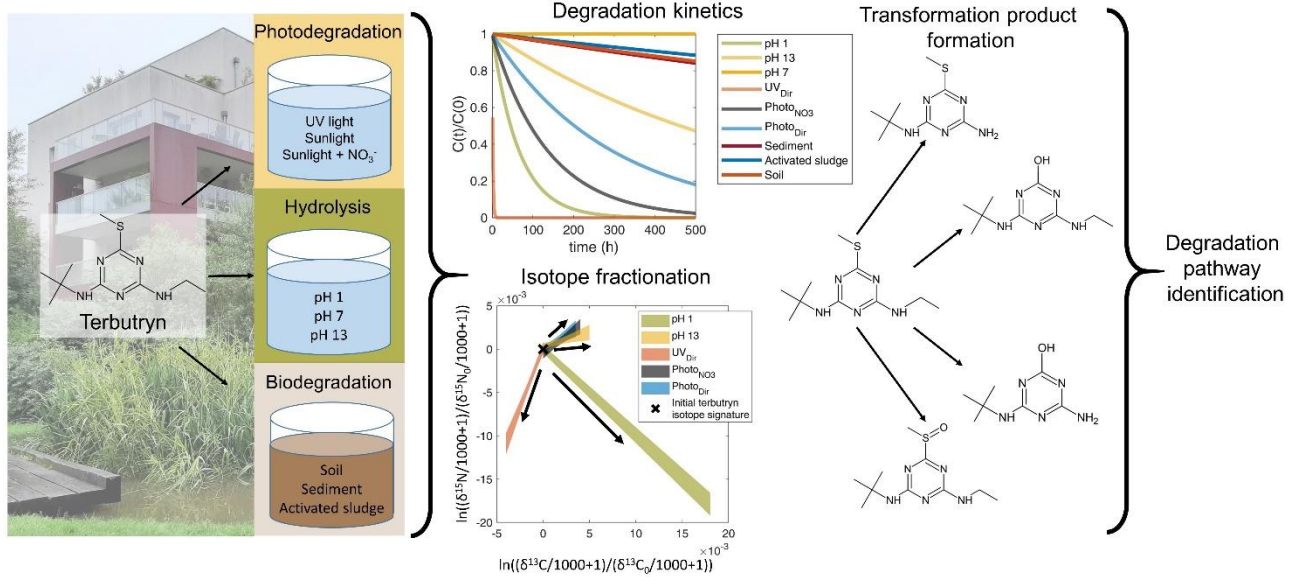
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20 **Graphical abstract**



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24 **Highlights**

- 25 • The biocide terbutryn released from building facades can contaminate soil and water
- 26 • Laboratory microcosms to examine terbutryn hydrolysis, photo- and bio-degradation
- 27 • Terbutryn degradation half-lives are high under environmental conditions
- 28 • Transformation products and CSIA of terbutryn to identify degradation pathways
- 29 • Differentiation of terbutryn degradation pathways based on dual-isotope values ($\Delta^{N/C}$)

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33

34 **Abstract**

35 Terbutryn is a widely used biocide in construction materials like paint and render to
36 prevent the growth of microorganisms, algae and fungi. Terbutryn is released from the
37 facades into the environment during rainfall, contaminating surface waters, soil and
38 groundwater. Knowledge of terbutryn dissipation from the facades to aquatic ecosystems is
39 scarce. Here, we examined in laboratory microcosms degradation half-lives, formation of
40 transformation products and carbon and nitrogen isotope fractionation during terbutryn direct
41 (UV light with $\lambda = 254$ nm and simulated sunlight) and indirect (simulated sunlight with
42 nitrate) photodegradation, abiotic hydrolysis (pH = 1, 7 and 13), and aerobic biodegradation
43 (stormwater pond sediment, soil and activated sludge). Biodegradation half-lives of terbutryn
44 were high (>80 d). Photodegradation under simulated sunlight and hydrolysis at extreme pH
45 values indicated slow degradability and accumulation in the environment. Photodegradation
46 resulted in a variety of transformation products, whereas abiotic hydrolysis lead solely to
47 terbutryn-2-hydroxy in acidic and basic conditions. Biodegradation indicates degradation to
48 terbutryn-2-hydroxy through terbutryn-sulfoxide. Compound-specific isotope analysis (CSIA)
49 of terbutryn holds potential to differentiate degradation pathways. Carbon isotope
50 fractionation values (ϵ_C) ranged from -3.4 ± 0.3 ‰ (hydrolysis pH 1) to $+0.8 \pm 0.1$ ‰
51 (photodegradation under UV light), while nitrogen isotope fractionation values ranged from $-$
52 1.0 ± 0.4 ‰ (simulated sunlight photodegradation with nitrate) to $+3.4 \pm 0.2$ ‰ (hydrolysis at
53 pH 1). In contrast, isotope fractionation during biodegradation was insignificant. $\Delta^{N/C}$ values
54 ranged from -1.0 ± 0.1 (hydrolysis at pH 1) to 2.8 ± 0.3 (photodegradation under UV light),
55 allowing to differentiate degradation pathways. Combining the formation of transformation
56 products and stable isotope fractionation enabled identifying distinct degradation pathways.
57 Altogether, this study highlights the potential of CSIA to follow terbutryn degradation *in situ*

58 and differentiate prevailing degradation pathways, which may help to monitor urban biocide
59 remediation and mitigation strategies.

60 **Keywords:** CSIA; Terbutryn; Hydrolysis; Photodegradation; Biodegradation; Transformation
61 products

62

63 **1. Introduction**

64 Biocides are added as in-can and film preservatives in building materials to prevent
65 algae and microbial growth on facade materials like paints and renders. During rainfall events,
66 biocides and their transformation products (TPs) are washed out from building materials and
67 enter into the environment (Bollmann et al., 2016; Burkhardt et al., 2012; Linke et al., 2021;
68 Schoknecht et al., 2009; Wittmer et al., 2011). Lab-scale experiments have demonstrated the
69 export of urban biocides from silicone render, acrylate render, roof paint and facade paints
70 (Burkhardt et al., 2012; Jungnickel et al., 2008; Schoknecht et al., 2009; Styszko et al., 2015).
71 However, knowledge of the contribution of dissipation processes controlling the reactive
72 transport of urban biocides from facades to surface waters, soil and groundwater remains
73 scarce.

74 Among urban biocides, an active compound of major concern is terbutryn, acting as a
75 photosynthesis inhibitor (Jurado et al., 2011). Terbutryn is still used as a pre-emergent or
76 post-emergent herbicide in agriculture in several countries (Carazo-Rojas et al., 2018;
77 LeBaron et al., 2008). In the EU, terbutryn is prohibited for agricultural applications since
78 2003 (European Council Directive 91/414/EEC, 2002) and is defined as a priority substance
79 since 2013 according to the Water Framework Directive (WFD) (European Council Directive
80 2013/39/EU, 2013). Terbutryn, measured in concentrations up to $5.6 \mu\text{g L}^{-1}$ in German rivers
81 exceeds predicted no-effect concentrations (PNEC, 0.003 to $0.034 \mu\text{g L}^{-1}$) (Burkhardt et al.,

82 2009; Kresmann et al., 2018; Quednow and Püttmann, 2007) and is detected in groundwater
83 (Hensen et al., 2018). The redundant detection of terbutryn in waters may be related to its low
84 removal in wastewater treatment plants (WWTP) (Luft et al., 2014; Paijens et al., 2021).
85 Altogether, this emphasizes significant, and possibly ecotoxic, release of terbutryn into
86 surface water. However, the contribution of degradative processes (i.e., photodegradation,
87 hydrolysis and biodegradation) and non-degradative process (i.e., sorption and dilution) to the
88 overall dissipation of terbutryn and its TPs is largely unknown.

89 *Photodegradation* may either occur directly on the facades or in water bodies, such as
90 retention ponds or rivers (Bollmann et al., 2016; Minelgaite et al., 2017; Sakkas et al., 2006;
91 Urbanczyk et al., 2019). Direct photodegradation refers to the absorption of light by a
92 molecule leading to bond cleavage, whereas indirect photodegradation results from the
93 excitation of other molecules, e.g. nitrate or dissolved organic carbon (DOC), and the
94 formation of radical reactive species mediating bond cleavages (Schwarzenbach et al., 2005).
95 Terbutryn degrades in the range of sunlight wavelengths (Hensen et al., 2019), although
96 degradation is slow under environmental conditions (Minelgaite et al., 2017). Terbutryn
97 photodegradation occurred in paint and on facades under controlled laboratory conditions and
98 in the environment (Bollmann et al., 2016; Schoknecht et al., 2021; Urbanczyk et al., 2019).
99 Several TPs of terbutryn have been identified under irradiation with UV light (Hensen et al.,
100 2018) and under simulated sunlight during direct and indirect photodegradation in aqueous
101 solutions and on paint surfaces (Hensen et al., 2019; Urbanczyk et al., 2019). This raises the
102 issue of the formation of photodegradation TPs and their release from facades.

103 *Hydrolysis* is a major pathway of pesticide degradation, which can be abiotically or
104 biologically-mediated (Fenner et al., 2013), depending on pH and temperature (Mabey and
105 Mill, 1978). Some studies indicate only minor abiotic hydrolysis of other triazine pesticides,

106 such as atrazine, under moderate acidic or alkaline pHs and degradation mainly occurring at
107 extreme pHs (<4 or >12) (Masbou et al., 2018; Meyer et al., 2009; Torrentó et al., 2021).

108 *Biodegradation* of terbutryn may occur in soils collecting runoff from facades, in
109 WWTPs and in water bodies receiving discharges from separated sewers. Biodegradation
110 half-lives of terbutryn in laboratory soil microcosms ranged from 7 (32 °C, 10 % soil moisture
111 content) to 227 days (4°C with 10 % soil moisture content) (Lechón et al., 1997), and from
112 180 to 240 days in water with river sediment under aerobic conditions (Muir and
113 Yarechewski, 1982), and up to 650 days under anaerobic conditions (Talja et al., 2008).
114 Biodegradation in activated WWTP sludge resulted mainly in the formation of terbutryn-
115 sulfoxide (TerSO). TerSO was further degraded to the hydroxy-derivate terbutryn-2-hydroxy
116 (TerOH) under acidic conditions (Luft et al., 2014). TerSO prevailed in the early state of
117 degradation under aerobic soil biodegradation experiments, with declining concentrations
118 throughout the experiment. TerOH, desbutyl-2-hydroxy-terbutryn (TerDesBOH) and
119 desethyl-terbutryn (TerDesE) were gradually formed, with minor contribution of desethyl-2-
120 hydroxy-terbutryn (TerDesEOH) (Bollmann et al., 2017a). Although the occurrence of TPs in
121 the environment indicates terbutryn degradation, further TP degradation, sorption or dilution
122 may limit the identification and the quantification of specific transformation pathways.

123 In this context, following up changes of the stable isotope composition (natural isotope
124 abundance) of the residual, non-degraded fraction of a pollutant may help to evaluate
125 degradation without considering concentration data of parent compound or TPs (Alvarez-
126 Zaldívar et al., 2018; Elsner et al., 2012; Elsner and Imfeld, 2016; Schmidt et al., 2004).
127 Typically, light isotopes (e.g., ¹²C) need a lower activation energy for bond cleavage
128 compared to heavy isotopes (e.g., ¹³C), resulting in faster reaction times and enrichment of
129 heavy isotopologues in the non-degraded fraction (Elsner, 2010). In contrast, non-degradative
130 processes like sorption, dilution or advection generally cause insignificant isotope

131 fractionation (Höhener and Yu, 2012; Schüth et al., 2003). In particular, compound-specific
132 isotope analysis (CSIA) of pollutants may help to identify reaction pathways by measuring
133 changes in stable isotope ratios (e.g., $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$), which are often reaction-specific
134 (Alvarez-Zaldívar et al., 2018; Elsner, 2010; Elsner and Imfeld, 2016; Fischer et al., 2016;
135 Meyer et al., 2009; Torrentó et al., 2021). In some cases, changes in isotope ratios may be
136 related to the extent of degradation using isotope fractionation values (ϵ) that are typically
137 retrieved from laboratory experiments under controlled conditions (Coplen, 2011; Hoefs,
138 2015). While CSIA has been used to study transformation of similar triazine type herbicides,
139 such as atrazine and ametryn (Drouin et al., 2021; Hartenbach et al., 2008; Lihl et al., 2020;
140 Masbou et al., 2018; Meyer et al., 2009; Schürner et al., 2015; Torrentó et al., 2021), isotope
141 fractionation of terbutryn during degradation has not been examined yet.

142 The purpose of this study was to examine the degradation rates and stable isotope
143 fractionation during abiotic hydrolysis, biodegradation and photodegradation of terbutryn to
144 improve the interpretation of terbutryn degradation from the facades to sink ecosystems, such
145 as soil and groundwater, in urban settings. Different terbutryn degradation pathways may lead
146 to distinct patterns of TP formation and stable isotope fractionation. We thus examined the
147 reaction kinetic rate constants, the TP formation, and carbon and nitrogen CSIA data to
148 evaluate degradation pathways of terbutryn and the potential of CSIA to follow up terbutryn
149 degradation *in situ* and distinguish degradation processes.

150

151 **2. Material & Methods**

152 **2.1. Chemicals**

153 Solvents (dichloromethane (DCM) and n-Pentane) were HPLC-grade (>99.9 %) and
154 purchased from Sigma-Aldrich (St. Louis, MO, USE). Analytical standards with purity >98%
155 (terbutryn and alachlor D-13) were purchased from PESTANAL (St. Louis, MO, USA).

156 Standards of terbutryn TPs TerOH, TerDesE and TerDesEOH (purity >98 %) were purchased
157 from HPC Standards GmbH (Borsdorf, Germany), TerSO (purity >97%) was purchased from
158 MicroCombiChem GmbH (Wiesbaden, Germany). Water, acetonitrile and formic acid for
159 analysis with HPLC-MS were LC/MS grade (Biosolve, France). Buffer solutions were
160 prepared using DI-water (>18 M Ω), hydrochloric acid (37 %, AnalaR NORMAPUR),
161 potassium phosphate monobasic (>99.5 %, Sigma Aldrich), potassium chloride (>99.5 %,
162 VWR Chemicals BDH) and sodium hydroxide (>95 %, Sigma Aldrich). Nitrate solutions for
163 photodegradation experiments were prepared with calcium nitrate tetrahydrate (>99 %, Sigma
164 Aldrich).

165

166 2.2. Experimental setup

167 *Photodegradation experiment.* Photodegradation experiments in aqueous solutions
168 were conducted under UV irradiation (UV_{Dir}), under simulated sunlight in pure water
169 (Photo_{Dir}) and under simulated sunlight with 20 mg L⁻¹ nitrate (Photo_{NO3}) to mimic
170 environmental conditions in surface waters. UV_{Dir} was conducted using a temperature-
171 controlled black box with a low-pressure mercury lamp (Philipps, TUV 6W G6T5) providing
172 a single-band light at $\lambda = 254$ nm. Simulated sunlight was replicated using a QSUN XE-1 test
173 chamber (Q-LAB, Westlake, OH USA) with a xenon arc lamp and a daylight-Q filter with a
174 nominal cut-on at 295 nm. The irradiation intensity was set to 0.68 W/m²/nm at 340 nm which
175 matches best with maximum solar irradiation and represents an intensity of ≈ 1200 W/m²
176 integrated over all wavelengths (QSun/QLab, 2011). Initial terbutryn concentrations were 10
177 mg L⁻¹ in the aqueous solutions. Three independent beakers (50 mL beakers containing 40 mL
178 solution) for sacrificial sampling were prepared for each sampling. Additionally, dark controls
179 and process blanks were prepared for three successive samplings throughout the experiment.
180 Sample preparation and sampling are detailed in Table S1. The pH of aqueous solutions

181 containing mixtures of terbutryn and TPs in different proportion and in the relevant
182 concentration range (1 – 10 mg L⁻¹), with and without calcium nitrate tetrahydrate (Ca(NO₃)₂
183 · 4 H₂O), did not change significantly (7.0 ± 0.5) (Section SI 2.2).

184 *Hydrolysis experiment.* Hydrolysis experiments were carried out in triplicate in 400
185 mL Schott glass bottles under dark and sterile conditions. Three aqueous buffer solutions
186 were prepared with sterilized DI water at pH = 1, 7 and 13 and sterilized by filtration through
187 sterile 0.2 µm PTFE filters (Rotilabo®, Carl Roth®, France). Extreme pH values were chosen
188 to increase degradation kinetics and study reaction pathways and associated isotope
189 fractionation. Buffer solutions were spiked with terbutryn to a final concentration of 10 mg L⁻¹.
190 Additional process blanks without terbutryn were prepared for each pH and sampled three
191 times throughout the experiment. Solutions were incubated at 60 °C to accelerate the reaction.
192 The preparation of buffer solutions, sample preparation and sampling procedures are detailed
193 in Table S1 and S2.

194 *Biodegradation.* Terbutryn biodegradation in different systems exposed to biocide
195 effluent was examined in microcosm experiments: (i) water from stormwater retention pond
196 with 100 mg L⁻¹ of 2 mm-sieved pond sediment (PondSed), (ii) soil from a stormwater swale
197 system (soil) and (iii) activated sludge from WWTP diluted 1:10 (v:v) in milliQ water.
198 Composite samples (n>5 subsamples) of either soil, pond water or sediment exposed to facade
199 runoff through drainage pipes and surface flow were collected in the Aldelshoffen district in
200 Schiltigheim (Strasbourg Eurometropolis, Bas-Rhin, France) and the respective samples were
201 mixed together thoroughly. The activated sludge was collected in the main WWTPs of
202 Strasbourg, receiving diluted urban runoff through combined sewer systems. The frequent
203 exposure of sediment, soil and activated sludge to terbutryn from facade runoff may lead to
204 microbial adaptation and favor terbutryn biodegradation (Poursat et al., 2019; Spain et al.,

205 1980). The collection procedure and physico-chemical characteristics of the samples used in
206 the biodegradation experiments are detailed in the SI.

207 Aerobic biodegradation microcosms consisted in 50 mL vials crimped with
208 butyl/PTFE caps filled either with 30 mL of spiked stormwater retention pond water with
209 sediment, 30 mL spiked diluted sewage sludge or 5 g of spiked soil. A needle with a 0.2 μ m
210 syringe filter was stuck through the cap to maintain oxic conditions without water loss (Torabi
211 et al., 2020). For each soil sample, 5 g of soil were spiked with terbutryn, to reach a final
212 concentration of 120 μ g g⁻¹, adjusted to a water content of 40 % and thoroughly mixed.
213 Concentrations are representative for accumulation of terbutryn on small receiving surfaces
214 exposed to repeated facade runoff with emission rates of several mg m⁻² event⁻¹ (Bollmann et
215 al., 2017b, 2016; Burkhardt et al., 2012). Stormwater retention pond and activated sludge
216 samples were spiked with terbutryn at 10 mg L⁻¹ and divided into the different microcosms for
217 sacrificial sampling. Concentrations are representative for direct facade runoff from new
218 buildings (Bollmann et al., 2017b, 2016; Burkhardt et al., 2012). Process blanks without
219 terbutryn and sterile controls were prepared for all setups. Microcosms were incubated at
220 room temperature (21 °C) and constantly shaken on an orbital shaker at 120 rpm. During each
221 sampling time (Table S1), triplicate microcosms were retrieved for extraction and analysis.

222 **2.3. Terbutryn extraction and quantification**

223 Liquid samples were extracted using liquid-liquid extraction. Briefly, the entire
224 sample for biodegradation experiments and 30 mL for photodegradation experiments were
225 transferred into 40 mL amber glass vials and terbutryn was extracted with DCM (3 mL).
226 Samples were shaken (600 rpm) for 5 min, ultrasonicated for 15 min, shaken again for 5
227 seconds and centrifuged at 1500 rpm for 5 min. Solvent was recovered and the whole
228 procedure was repeated three times. The extracts were pooled and evaporated under gentle N₂
229 stream. Samples were resuspended in 0.5 mL DCM. Soil samples followed a modified solid-

230 liquid extraction with 3:1 Pentane:DCM (v:v) and purification procedure (Droz et al., 2021;
231 Ivdra et al., 2014). Water subsamples (1 mL) were collected at different time points and
232 filtered at 0.2 μm for TP analysis (Table S1 and sections SI 1.2 – SI 1.4). All samples were
233 stored in the freezer at -20°C until analysis. Recoveries of extraction methods and validation
234 for CSIA (i.e., absence of stable isotope fractionation associated with the methods) are
235 provided in SI (Section 1.5).

236 Terbutryn and four main TPs TerSO, TerOH, TerDesE and TerDesEOH (Table S5)
237 were quantified using ultra high-pressure liquid chromatography (UHPLC) (Dionex/ Thermo
238 Scientific UltiMate Dionex 3000) coupled to a triple quadrupole mass spectrometer (Thermo
239 Scientific TSQ Quantiva), using a C18 column (Accucore 100 x 2.1, particle size 2.6 μm).
240 Solvent gradients, mass transitions, LOQ and LOD are provided in SI (Table S6 and S7).

241 **2.4. Compound-specific isotope analysis**

242 Carbon and nitrogen stable isotope analysis was conducted using a GC/IRMS system
243 consisting of a gas chromatograph (GC, TRACE Ultra ThermoFisher Scientific) coupled to an
244 isotope ratio mass spectrometer (IRMS, DeltaV plus, ThermoFisher Scientific) via a GC
245 combustion interface (IsoLink/Conflow IV, ThermoFisher Scientific) equipped with a TG-
246 5MS column (60 m \times 0.25 mm ID, 0.25 μm film thickness). The samples (0.3 - 3 μL) were
247 injected via a split/splitless injector at 250°C with helium as carrier gas at a 1.5 mL min^{-1}
248 flow rate. The GC temperature program and quality controls are described in Section S1.9.
249 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values were calibrated against the VPDB and air standards, respectively, using
250 international reference materials AIEA600, USGS40 and USGS41. The range of the GC-
251 IRMS where isotope values are independent of signal intensity for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values (i.e.,
252 the range of injected amount of terbutryn for which carbon and nitrogen isotope values are
253 within a $\pm 0.5\text{ ‰}$ interval) was established for peak amplitudes from 220 to 2560 for $\delta^{13}\text{C}$
254 ($m/z = 44$), and from 220 to 1480 for $\delta^{15}\text{N}$ ($m/z = 28$) (Figure S2).

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258 **2.5. Data analysis**

259 For all degradation experiments, concentrations were plotted against experimental
260 time and fitted using first order degradation kinetics with Matlab R2020 b using the fit
261 function.

262 Isotope ratios were normalized to VPDB and air standards for carbon and nitrogen
263 stable isotopes respectively and written in the delta notation (Elsner, 2010):

$$\delta_{sample}E [‰] = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) \cdot 1000$$

264 The Rayleigh equation was used to calculate the isotope values of the residual (non-degraded)
265 fraction of terbutryn (Elsner, 2010):

$$\ln \left(\frac{R_{t,E}}{R_{0,E}} \right) = \ln \left(\frac{C_{t,E}}{C_{0,E}} \right) \cdot \frac{\epsilon_{bulk}^E}{1000}$$

266 Where $R_{t,E}/R_{0,E}$ is the isotope ratio of the element E (e.g. $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$), $C_{t,E}$ and $C_{0,E}$ are
267 concentrations of terbutryn at a specific time t and at the start of the experiment (0) and ϵ_{bulk}^E
268 is the apparent isotope fractionation value. Apparent isotope values were derived from linear
269 regression by taking into account each of the triplicate microcosms/samples individually
270 (Scott et al., 2004). Given uncertainties correspond to the 95 % confidence interval (CI) of the
271 slope of the linear regression. $\Lambda^{N/C}$ values were derived using the York regression, accounting
272 for uncertainties in C and N isotope measurements (Höhener and Imfeld, 2021; Ojeda et al.,
273 2019) according to:

$$\Lambda^{N/C} = \frac{\ln \left[\left(\frac{\delta^{15}N_t}{1000} + 1 \right) / \left(\frac{\delta^{15}N_0}{1000} + 1 \right) \right]}{\ln \left[\left(\frac{\delta^{13}C_t}{1000} + 1 \right) / \left(\frac{\delta^{13}C_0}{1000} + 1 \right) \right]}$$

274 For analysis of $\Lambda^{N/C}$ values, the R package IsoplotR was used (Vermeesch, 2018).

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279 3. Results

280 3.1. Terbutryn photodegradation

281 Terbutryn photodegradation was faster under UV light than under simulated sunlight
282 (Table 1), due to the absorption spectrum of terbutryn and irradiation intensity (Bollmann et
283 al., 2016; Hensen et al., 2019; Minelgaite et al., 2017). Slower terbutryn degradation under
284 simulated sunlight likely reflects the slight overlap of the absorption spectrum of terbutryn
285 with simulated sunlight at wavelengths 290 – 300 nm (SI, Figure S4). Selecting a
286 representative irradiation source, such as a filtered Xenon arc lamp, is thus crucial to infer
287 environmentally relevant photodegradation kinetics, especially for compounds weakly
288 absorbing sunlight, such as terbutryn (Hensen et al., 2019).

289
290 Table 1. Terbutryn degradation half-life ($t_{1/2}$) and degradation rate constant (k), isotope
291 fractionation values for carbon (ϵ_C) and nitrogen (ϵ_N) and $\Lambda^{N/C}$ values. Uncertainties are given
292 as 95% confidence interval (\pm 95% CI). NS: non-significant degradation or isotope
293 fractionation ($\Delta\delta^{13}C$ or $\Delta\delta^{15}N < 0.5$ ‰ in biodegradation experiments).

	Degradation process	$t_{1/2}$	k [s^{-1}]	ϵ_C [‰]	ϵ_N [‰]	$\Lambda^{N/C}$
UV _{Dir}	Photodegradation	68.7 ± 24.6 min	$1.7 \times 10^{-4} \pm 9.4 \times 10^{-5}$	+0.8 ± 0.1	+2.2 ± 0.3	2.8 ± 0.3
Photo _{NO3}		93.6 ± 37.2 h	$2.1 \times 10^{-6} \pm 1.4 \times 10^{-6}$	-0.6 ± 0.2	-1.0 ± 0.4	0.8 ± 0.1
Photo _{Dir}		202.3 ± 83.3 h	$9.5 \times 10^{-7} \pm 6.7 \times 10^{-7}$	-0.7 ± 0.3	-0.5 ± 0.3	0.7 ± 0.2

pH 1	Abiotic Hydrolysis	45.4 ± 15.2 h	4.2×10 ⁻⁶ ± 2.1×10 ⁻⁶	-3.4 ± 0.3	+3.4 ± 0.2	-1.0 ± 0.1
pH 7		NS	NS	NS	NS	NS
pH 13		462.3 ± 173.3 h	4.2×10 ⁻⁷ ± 2.5×10 ⁻⁷	-1.3 ± 0.2	-0.4 ± 0.3	0.3 ± 0.1
Pond + sediment	Biodegradation	83.6 ± 27.6 d	9.6×10 ⁻⁸ ± 4.7×10 ⁻⁸	NS	NS	NS
Soil		90.2 ± 34.5 d	8.9×10 ⁻⁸ ± 5.5×10 ⁻⁸	NS	NS	NS
Activated sludge		117.1 ± 34.4 d	6.9×10 ⁻⁸ ± 2.9×10 ⁻⁸	NS	NS	NS

294

295 Photodegradation rate constants were twice higher with than without nitrate (Table 1).

296 Nitrate concentrations are often above 20 mg/L in agricultural surface waters as well as

297 effluents of WWTPs, where urban biocides are present as well. Irradiation of nitrate may form

298 hydroxy radicals ($NO_3^- + H_2O \xrightarrow{hv} NO_2 + OH \cdot + OH$) acting as photocatalyst during

299 indirect photodegradation of terbutryn (Schwarzenbach et al., 2005). Hence, terbutryn

300 degradation rate constants increase with increasing formation of hydroxy radicals (Hensen et

301 al., 2019; Lam et al., 2003). It is worth mentioning, that direct and indirect photodegradation

302 can co-occur in water, limiting the estimation of the contribution of nitrate-mediated

303 degradation. Direct and indirect terbutryn photodegradation may also already occur on

304 facades (Bollmann et al., 2016; Schoknecht et al., 2021; Urbanczyk et al., 2019) then in sink

305 aquatic ecosystems, including storm water retention systems (swale systems), rivers and lakes

306 where terbutryn was frequently detected (Ccanccapa et al., 2016; Linke et al., 2021; Machate

307 et al., 2021; Quednow and Püttmann, 2007). Besides nitrate, other substances (e.g. humic

308 acids or dissolved organic matter) can catalyze photodegradation by providing radicals or

309 decelerate photodegradation through absorption and shielding of the contaminant (Drouin et

310 al., 2021; Wu et al., 2021; Zhang et al., 2015). Degradation kinetics, however, may be

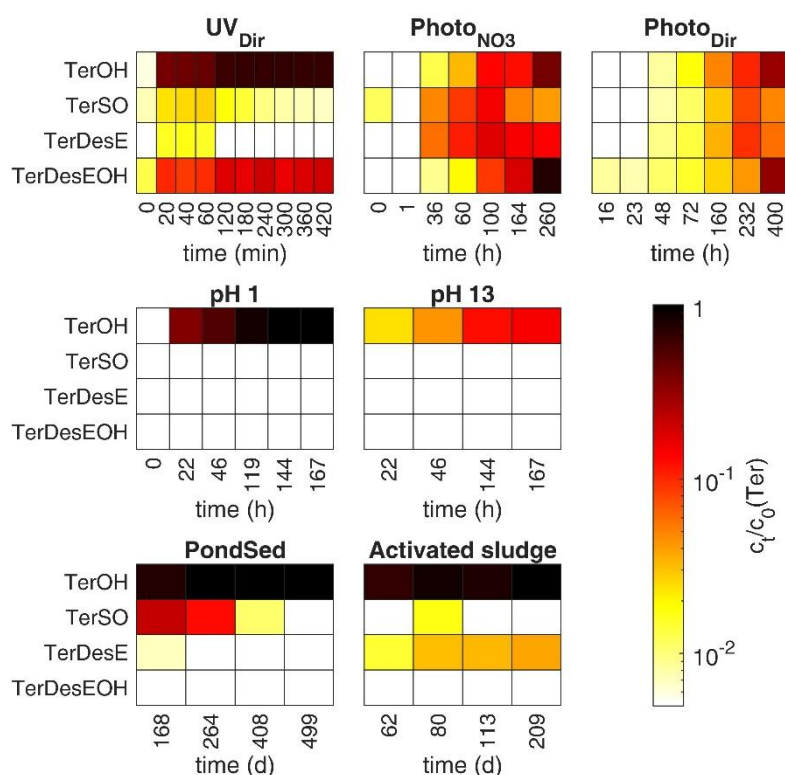
311 overestimated as they represent constant irradiation with light intensities of peak natural

312 daylight (CIE, 1989; QSun/QLab, 2011). Considering the mean annual solar surface
313 irradiation in northern Europe (100 – 200 W/m², accounting for e.g. diurnal and annual
314 variation) (Pfeifroth et al., 2018), photodegradation half-lives in the environment may
315 increase by one order of magnitude compared to half-lives estimated in the laboratory
316 experiments.

317 TerOH mainly formed during photodegradation under UV light, followed by
318 TerDesEOH. In contrast, TerSO and TerDesE concentrations initially increased and gradually
319 decreased during the experiment (Figure 1). Similar trends were observed during
320 photodegradation under artificial sunlight (Figure 1). For UV light induced transformation,
321 TerOH was formed either through substitution of the methylthio group by a hydroxy group
322 through hydroxy radicals, or through an oxidation of the methylthio group, leading to TerSO,
323 and further substitution of the oxidized methylthio group by a hydroxy group. This is
324 supported by an increase of TerSO concentrations, followed by TerSO depletion (Figure 1). A
325 similar pattern was observed for TerDesE formation through the loss of an ethyl group at the
326 side chain of terbutryn. TerDesEOH was likely formed through TerDesE by a cleavage of the
327 methylthio group and substitution through a hydroxy group. In contrast, the formation of
328 TerDesEOH through TerOH is unlikely as supported by constant TerOH concentrations up to
329 the end of the experiment. Desthiomethyl-terbutryn (TerDesS, Table S5) was previously
330 identified as a main TP formed through the loss of the -SCH₃ sidechain during
331 photodegradation under UV irradiation (Bollmann et al., 2016 and Hensen et al., 2018).
332 Although the contribution of TerDesS to the overall mass balance could not be quantified in
333 our experiment due to the lack of an analytical standard, it was likely limited as the mass
334 balance was nearly closed (>80 % recovery) with TerOH, TerDesEOH, TerSO and TerDesE.

335 The dominant TPs in photodegradation experiment with simulated sunlight were
336 TerDesEOH, TerOH, with lower and decreasing concentrations of TerDesE and TerSO at the

337 end of the experiment. TP patterns were similar in experiments with nitrate and distilled
 338 water. The dominance of terbutryn hydroxylation and/or dealkylation pathways suggest
 339 similar degradation patterns during direct and indirect photodegradation (Burrows et al., 2002;
 340 Hensen et al., 2019). However, on paint surfaces, TP formation patterns in photodegradation
 341 assays with UVB irradiation suggested a dependency on pigments and polymers that can get
 342 excited and cause indirect photodegradation (Urbanczyk et al., 2019). In pigment free paint,
 343 where most degradation occurred, TerSO increased before gradually decreasing, whereas
 344 TerDesEOH steadily increased, while TerOH concentrations reached a constant level
 345 (Urbanczyk et al., 2019). This latter pattern of TP formation is coherent with that of our study
 346 (Figure 1), highlighting the relevance to consider transformation processes on the facades.



347
 348 Figure 1. Transformation products formed during terbutryn photodegradation (top), abiotic
 349 hydrolysis (middle) and biodegradation (bottom). Results are given in molar concentrations
 350 normalized to the initial concentration of terbutryn (ter). No degradation was observed at pH

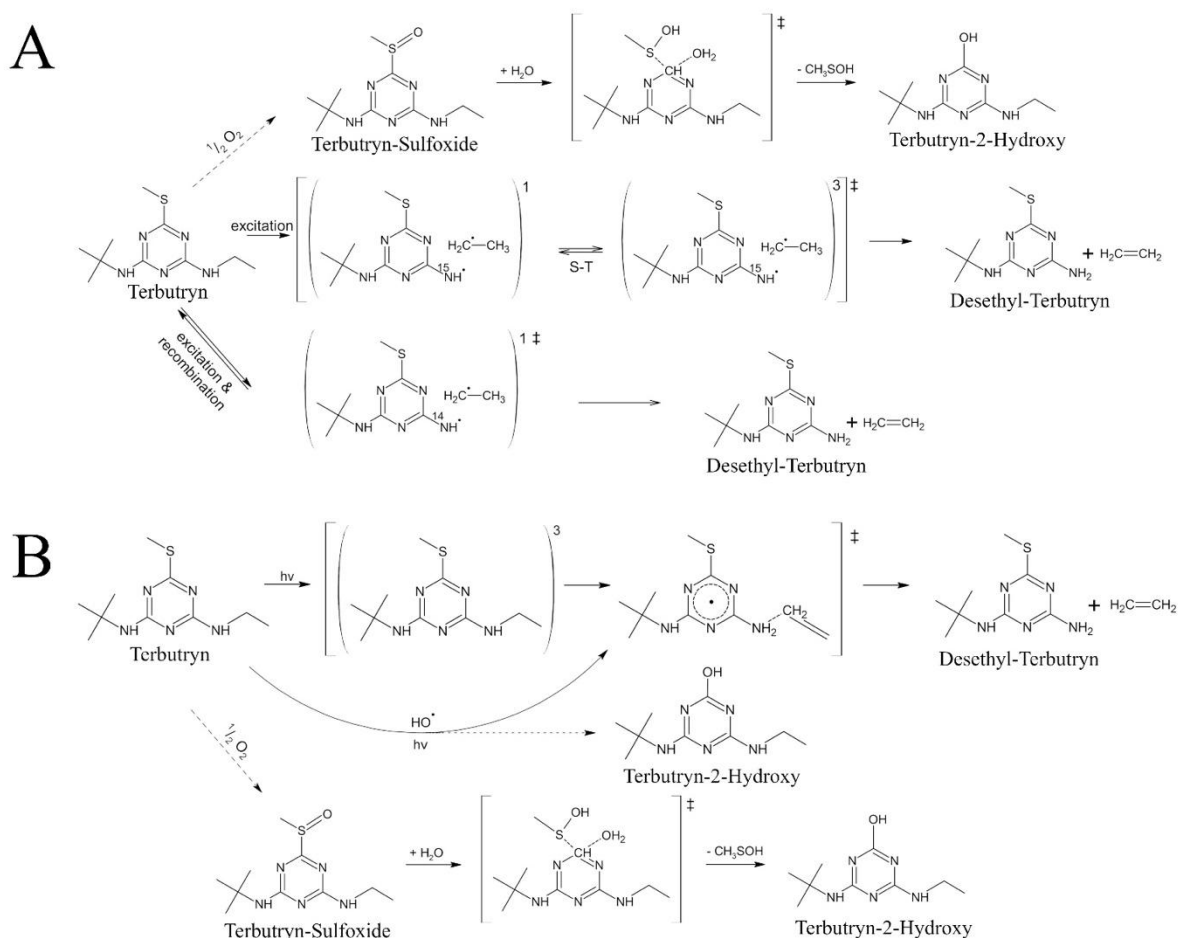
351 7. Transformation products in soil microcosms were only measured for one sampling (Figure
352 S5).

353

354 Carbon and nitrogen stable isotope fractionations differed for photodegradation under
355 UV light and with simulated sunlight but were similar for direct and indirect photodegradation
356 under simulated sunlight. Photodegradation under UV light resulted in inverse isotope
357 fractionation values, i.e., an enrichment of light isotopes in non-degraded fraction, for both
358 carbon ($\epsilon_C = +0.8 \pm 0.10 \text{ ‰}$) and nitrogen ($\epsilon_N = +2.2 \pm 0.3$). In contrast, simulated sunlight
359 resulted in normal isotope fractionation (Table 1, Figure S6 and S7).

360 An inverse isotope effect for triazine transformation by UV light was related to
361 excitation and relaxation processes or magnetic isotope effects (Drouin et al., 2021;
362 Hartenbach et al., 2008; Knossow et al., 2020). An inverse isotope fractionation value during
363 photodegradation under UV light was previously observed for atrazine, with a similar isotope
364 fractionation value for nitrogen ($\epsilon_{N(\text{Atrazine})} = +2.4 \pm 0.3 \text{ ‰}$) and more pronounced effect for
365 carbon ($\epsilon_{C(\text{Atrazine})} = +2.7 \pm 0.3 \text{ ‰}$) compared to isotope fractionation values for terbutryn
366 degradation (Drouin et al., 2021; Hartenbach et al., 2008). A less pronounced carbon isotope
367 fractionation during terbutryn degradation suggests terbutryn degradation to TerSO and then
368 to TerOH, rather than the direct formation of TerOH. This idea is also supported by
369 decreasing TerSO concentrations. The formation of TerSO may not significantly affect carbon
370 or nitrogen isotope fractionation since carbon and nitrogen are not directly involved in bond
371 cleavage or formation. In addition, constant TerOH concentrations indicate the formation of
372 TerDesEOH through TerDesE rather than through TerOH. An inverse isotope fractionation
373 may thus be caused by excitation at the triazine ring (Figure 2 A). The excitation may result in
374 the formation of the singlet state and conversion to the triplet state with cleavage of the C-N

375 bond, e.g., during the formation of TerDesE. During the transition state, the bond is either
 376 cleaved or the molecule recombines. A recombination of the initial molecule is likelier for
 377 bonds containing light isotopes, resulting in enrichment of the light isotope in the non-
 378 degraded fraction. In addition, isotope fractionation may be more pronounced for nitrogen
 379 than for carbon, due to dilution effect for carbon isotopes.



380
 381 Figure 2. Suggested pathways for photodegradation of terbutryn under UV irradiation ($\lambda =$
 382 254 nm) (A) and under simulated sunlight (B) modified from Knossow et al., 2020. Numbers
 383 at the brackets represent the singlet (1) or triplet (3) state of the molecule. The double-cross
 384 (\ddagger) indicates the transition state. The dashed arrow in the reaction to TerSO implies that no
 385 Carbon or Nitrogen isotope fractionation is expected.

386

387 In contrast, simulated sunlight resulted in an enrichment of ^{13}C and ^{15}N in the non-
388 degraded fraction of terbutryn in both direct ($\epsilon_{\text{C}} = -0.7 \pm 0.3 \text{ ‰}$ and $\epsilon_{\text{N}} = -0.5 \pm 0.3$) and
389 indirect ($\epsilon_{\text{C}} = -0.6 \pm 0.2 \text{ ‰}$ and $\epsilon_{\text{N}} = -1.0 \pm 0.4$) experiments. Although several reactions may
390 occur simultaneously during irradiation with sunlight, reaction mechanisms and associated
391 isotope fractionation have been rarely examined. We hypothesize that degradation through
392 TerSO to TerOH may occur under simulated sunlight with and without nitrate, causing
393 insignificant carbon or nitrogen isotope fractionation as neither carbon nor nitrogen atoms are
394 involved in bond cleavage. On the other hand, the formation of TerDesE and TerDesEOH
395 suggests the excitation and the formation of a triplet state intermediate, which is further
396 transformed into a terbutryn radical. The terbutryn radical might be delocalized over the
397 aromatic ring as previously described for bromoxynil (Knossow et al., 2020), and weaken the
398 C-N bond. This would result in bond cleavage during the formation of TerDesE through
399 desethylation, causing normal isotope fractionation (Figure 2B). Worthy of note, the direct
400 formation of TerOH in the presence of OH^{\bullet} radicals (e.g., through excitation of nitrate) during
401 indirect photodegradation cannot be excluded, however a deviation from isotope fractionation
402 values of direct photodegradation would be expected.

403

404 **3.2. Terbutryn hydrolysis**

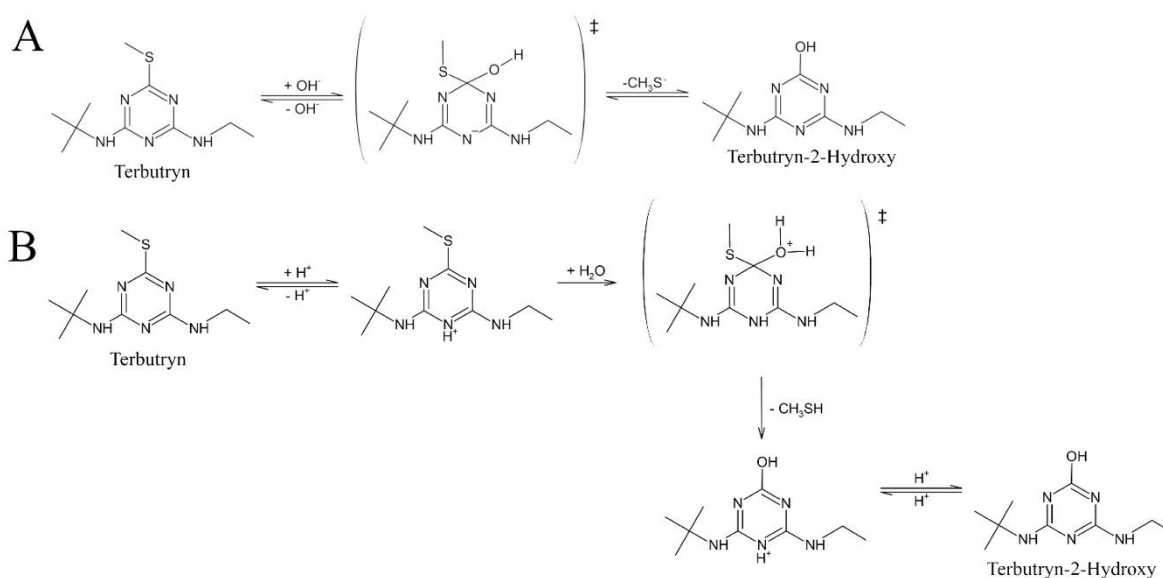
405 Overall, our results emphasize limited hydrolysis of terbutryn under most common
406 environmental conditions. Terbutryn hydrolysis occurred at $\text{pH} = 1$ and $\text{pH} = 13$ but was
407 insignificant at $\text{pH} = 7$ (Table 1). Acidic hydrolysis at $\text{pH} = 1$ was ten times faster than
408 hydrolysis at $\text{pH} = 13$. Acidic hydrolysis occurs through bond cleavage catalyzed by H^+ ,
409 whereas hydrolysis at $\text{pH} 13$ occurs through a base mediated reaction with OH^- as nucleophile
410 (Wolfe et al., 1990).

411 Studies on hydrolysis of terbutryn are scarce, although previous studies on triazine
412 pesticides indicated high hydrolytic stability between pH = 5 and pH = 9 (Lewis et al., 2016;
413 Masbou et al., 2018), slow degradation at pH < 4 and insignificant degradation at pH = 7 and
414 pH = 9 (Comber, 1999). While acidic rain (pH ~5; Keresztesi et al., 2019) may slightly
415 hydrolyze terbutryn in facade runoff, surface waters in Europe and Northern America
416 typically have higher pH values (Austnes et al., 2018). Alkaline pH values are rarely observed
417 in the environment but might occur, for example, in soda lakes (pH >10) (Grant and Sorokin,
418 2011) or directly in the pores of facade material (pH = 9.5) (Styszko et al., 2014). Overall, our
419 results indicate that the contribution of hydrolysis to the overall terbutryn degradation is
420 limited under typical environmental pH values and temperatures.

421 Only TerOH was detected during abiotic hydrolysis at pH = 1 and pH = 13, indicating
422 nucleophile substitution of the methylthio group under alkaline conditions (pH = 13) (Figure
423 3 A). Under acidic conditions, we hypothesize an intermediate step through the protonation of
424 the triazine ring followed by the cleavage of the SCH₃ group, as suggested for atrazine
425 (Meyer et al., 2009; Russell et al., 1968 Meyer et al., 2008), and in agreement with the
426 formation of TerOH during terbutryn acidic hydrolysis (Figure 3B).

427 Although TerOH was formed during both alkaline and acidic hydrolysis of terbutryn,
428 carbon and nitrogen isotope fractionation significantly differed, indicating distinct
429 degradation pathways (Table 1, Figure 1). Under alkaline hydrolysis, isotope fractionation
430 was observed for carbon ($\epsilon_C = -1.3 \pm 0.2$), and to lesser extent for nitrogen ($\epsilon_N = -0.4 \pm 0.3$).
431 The carbon isotope fractionation may be due to nucleophilic substitution of the methylthio
432 group during the formation of TerOH. The less pronounced nitrogen fractionation likely
433 results from a secondary isotope effect since no N atom is directly involved in the bond
434 cleavage (Figure 3 A). In contrast, acidic hydrolysis resulted in a normal isotope fractionation
435 for carbon ($\epsilon_C = -3.4 \pm 0.7$) and an inverse isotope fractionation for nitrogen ($\epsilon_N = +3.4 \pm 0.1$).

436 Protonation of a nitrogen atom in the triazine ring is leading to a polarization of the C-SCH₃
 437 bond and the formation of TerOH (Figure 3 B). The bond cleavage at the methylthio group is
 438 expected to result in carbon isotope fractionation, as previously described for atrazine
 439 (Masbou et al., 2018; Meyer et al., 2009). Protonation of a nitrogen atom in the triazine ring
 440 would lead to an inverse isotope effect for nitrogen, as observed in this study. Such bonding is
 441 more stable for heavy isotopes in the transition state, resulting in an enrichment of light
 442 isotopes in the non-degraded fraction. Even though extreme pH values are unlikely to occur in
 443 the environment, slower degradation at less extreme pHs might result in similar TP formation
 444 and isotope fractionation since the reaction pathway is identical.
 445



447 *Figure 3. Suggested pathways of terbutryn transformation during abiotic hydrolysis at pH 13*
 448 *(A) and pH 1 (B) (modified from Meyer et al., 2009). The double-cross (\ddagger) indicates the*
 449 *transition state.*

450 3.3. Terbutryn biodegradation

451 Half-lives for terbutryn biodegradation, ordered from the lowest to the highest half-
 452 lives: PondSed<Soil<activated sludge, were 4 to 62-fold higher than half-lives for terbutryn

453 photodegradation under simulated sunlight and hydrolysis (Table 1). However,
454 biodegradation rates and sunlight induced degradation of terbutryn may be in the same order
455 of magnitude since environmental photodegradation half-lives were overestimated in our
456 study as previously discussed in section 3.1.

457 Overall, these results suggest slow terbutryn biodegradation in the environment.
458 Microbial adaptation may explain faster terbutryn degradation in pond-sediment and soil
459 experiments than in the activated sludge experiment (Poursat et al., 2019; Spain et al., 1980).
460 Indeed, pond water and sediment in the PondSed, and soil in the soil experiments, were
461 chronically exposed to direct release of terbutryn from facades at the sampling site. It is also
462 worth noting that a wide range of half-lives (7 up to >240 days) for terbutryn degradation in
463 previous laboratory studies underscores a strong dependency on the incubation method and
464 matrix (Bollmann et al., 2017a; Lechón et al., 1997; Muir and Yarechewski, 1982). Half-lives
465 for terbutryn degradation in activated WWTP sludge were two orders of magnitude higher
466 than those in previous experiments with activated sewage sludge (2.1 to 7 days) (Luft et al.,
467 2014). The initial amount and activity of degrading microorganisms in activated sewage
468 inoculum may strongly vary among experiments, thereby affecting terbutryn degradation
469 kinetics. In general, terbutryn degradation in WWTPs is expected to be limited as hydraulic
470 retention times in WWTPs (<24 h) are typically lower than half-lives (Verlicchi et al., 2012).
471 Terbutryn and other urban biocides were frequently detected in effluents and downstream of
472 WWTPs, underlining the limited degradation in treatment facilities (Le et al., 2017; Paijens et
473 al., 2021).

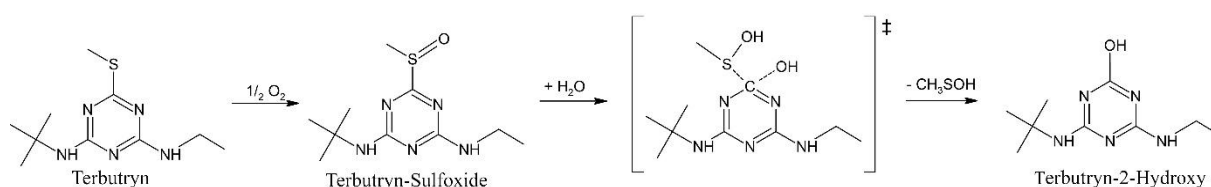
474 TerOH was the prevailing TP formed during biodegradation (Figure 1). TPs in soil
475 microcosm experiments were only measured at one time point (Figure S5). We hypothesize
476 that terbutryn degraded to TerSO, which was further degraded to TerOH (Luft et al., 2014).
477 The degradation of methylthio-s-triazines through sulfoxides to the respective hydroxyl

478 derivates has been described previously (Kaufman and Kearney, 1976), and confirmed in
 479 degradation experiments with *Bacillus cereus* strain JUN7 (Harada et al., 2006). The
 480 prevalence of biodegradation via TerSO is also supported in our experiment by decreasing
 481 TerSO concentrations in sediment microcosms (PondSed), coinciding with increasing TerOH
 482 concentrations. A similar trend was observed in soil biodegradation experiments, alongside
 483 the formation of other TPs, including Desbutyl-2-hydroxy-terbutryn through a dealkylation of
 484 the TerOH sidechain (Bollmann et al., 2017a).

485 Terbutryn biodegradation did not lead to significant carbon and nitrogen stable isotope
 486 fractionation ($\Delta\delta^{13}\text{C}$ and $\Delta\delta^{15}\text{N} < 0.5\text{‰}$) (Table 1). This further supports the hypothesis of an
 487 initial terbutryn degradation to TerSO, although TerOH was the main TP detected during
 488 biodegradation. Indeed, the oxidation of the methylthio group to form TerSO could only lead
 489 to a secondary carbon or nitrogen isotope effect since carbon or nitrogen are not directly
 490 involved in bond cleavage (Figure 4). Further transformation from TerSO to TerOH is not
 491 affecting terbutryn stable isotope composition.

492 Altogether, both CSIA and TP data confirmed that degradation through the sulfoxide
 493 to the 2-hydroxy derivate is a major biodegradation pathway of terbutryn, in agreement with
 494 previous studies (Harada et al., 2006; Luft et al., 2014).

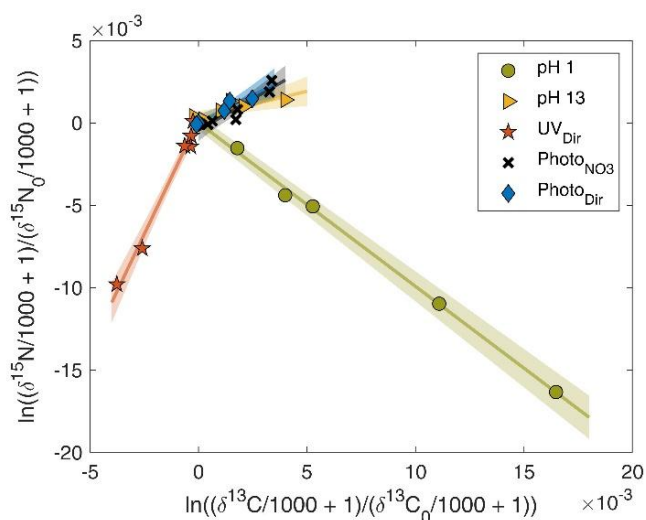
495



497 Figure 4. Suggested pathway of terbutryn biodegradation. The double-cross (\ddagger) indicates the
 498 transition state.

500 3.4. Contribution of terbutryn degradation pathways in the environment

501 The dual carbon and nitrogen isotope plot shows that stable isotope fractionation
 502 patterns may help differentiate degradation pathways of terbutryn in the environment (Figure
 503 5). This is relevant since classical concentration-based approaches cannot tease apart the
 504 contribution of sorption, dilution and degradation to the overall terbutryn dissipation. While
 505 single element CSIA provides a footprint of degradation when isotope values change due to
 506 kinetic isotope effect, distinct degradation pathways often occur simultaneously or
 507 consecutively, and thus may be mistaken. For instance, terbutryn direct photodegradation on
 508 facades may be followed by biodegradation in soil, and indirect photodegradation in a river or
 509 storm water retention pond.



510

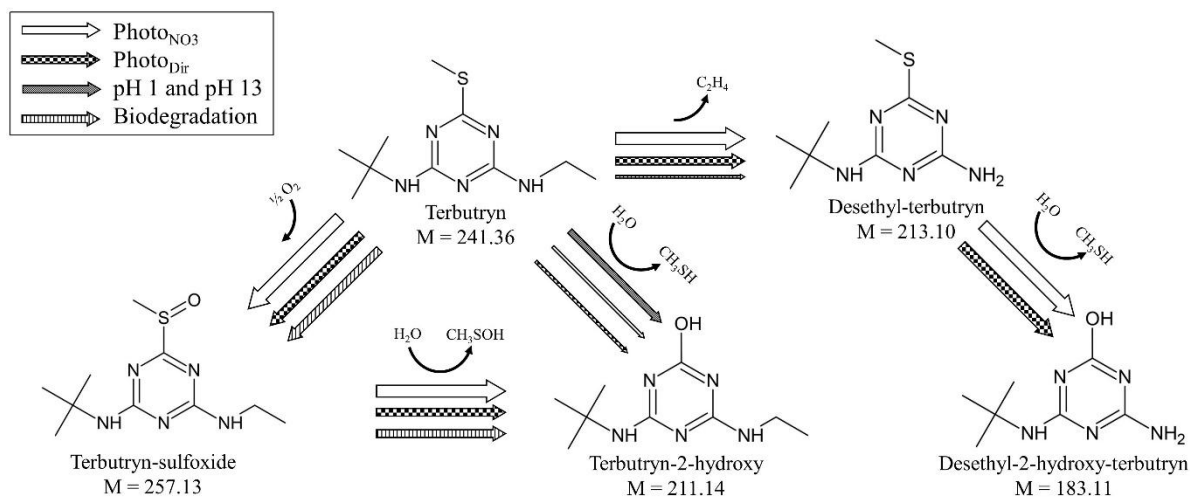
511 Figure 5. Dual C and N isotope plot for terbutryn degradation. Stable isotope fractionation
 512 patterns are represented at pH 1 (green circles), pH 13 (yellow triangles), irradiation with UV
 513 light (orange stars), irradiation under simulated sunlight in presence of nitrate (black crosses)
 514 and irradiation under simulated sunlight in pure water (blue diamonds). Shaded areas
 515 represent the 95 % confidence interval (CI) according to the York method (Ojeda et al.,
 516 2019). The origin (0,0) represents the original terbutryn isotope signature prior to degradation.

517

518 In this case, the dual element plot representing $\delta^{15}\text{N}$ against $\delta^{13}\text{C}$ values may help to
519 identify degradation pathways of terbutryn. For instance, $\Lambda^{\text{N/C}}$ patterns for terbutryn
520 photodegradation under UV light and with simulated sunlight indicate distinct transformation
521 pathways (Figure 5). Hence, terbutryn photodegradation experiments under UV light have
522 limited value to evaluate environmental photo-transformation because pathways differ from
523 natural sunlight conditions but can be used to follow UV based remediation processes of
524 water and wastewater (Yang et al., 2014). On the other hand, isotope fractionation patterns
525 during direct and indirect terbutryn photodegradation are similar under simulated sunlight.
526 This emphasizes that carbon and nitrogen stable isotope fractionation may help to distinguish
527 terbutryn photodegradation from biodegradation or hydrolysis in environmental studies.
528 However, the contribution of direct and indirect photodegradation may not be differentiated
529 using carbon and nitrogen CSIA (Figure 5).

530 In addition, the direction and extent of isotope fractionation may indicate underlying
531 reactions, reflecting degradation mechanisms, as shown for $^{15}\text{N}/^{14}\text{N}$ in terbutryn. Although
532 TerOH is formed during both alkaline and acidic hydrolysis, the dual isotope plot highlights
533 that the underlying degradation mechanisms differ substantially for abiotic acidic ($\Lambda^{\text{N/C}} = -1.0$
534 ± 0.1) and alkaline ($\Lambda^{\text{N/C}} = 0.3 \pm 0.1$) hydrolysis of terbutryn (Figure 5). For instance, an
535 unusual trend to more negative $\delta^{15}\text{N}$ values (inverse isotope effect) occurs during protonation
536 of the nitrogen atoms during acidic hydrolysis as ^{15}N protonation is more stable than ^{14}N in
537 the transition state. In contrast, the nucleophilic substitution of the methylthio group during
538 alkaline hydrolysis of terbutryn results in normal isotope effect. This highlights the reaction
539 specificity of multi element (ME) CSIA to identify degradation mechanisms, even when the
540 same TP is eventually formed.

541 Altogether, combining TP analysis with carbon and nitrogen isotope CSIA allows to
 542 identify and compare pathways of terbutryn photodegradation under UV and simulated
 543 sunlight irradiation, abiotic acidic and alkaline hydrolysis and biodegradation (Figure 6).



544
 545 Figure 6. Putative degradation pathways of terbutryn in the environment. The thickness of the
 546 arrows indicates the contribution of each process to the overall degradation. Thick arrows
 547 indicate the main contribution while thinner arrows indicate minor contribution of the
 548 respective degradation pathway to the overall terbutryn transformation.

549
 550 **Conclusion**

551 Better knowledge of degradation kinetics and pathways of terbutryn in different
 552 environmental compartments may help to evaluate the terbutryn reactive transport across the
 553 facade-soil-water continuum. Our results emphasize that photodegradation may contribute to
 554 terbutryn degradation on the facade and in waters. Since setups and irradiation intensities of
 555 simulated sunlight experiments require correction for the local irradiation intensities,
 556 degradation rates indicate further terbutryn accumulation in the environment. Terbutryn
 557 released from facades during rainfall events may accumulate in soil receiving facade wash-off
 558 due to limited terbutryn biodegradation and hydrolysis. In particular, the contribution of

559 abiotic hydrolysis to terbutryn degradation appears negligible under most environmental
560 conditions.

561 Most importantly, the combination of ME-CSIA data and TP quantification allowed to
562 identify and tease apart degradation pathways of terbutryn. While terbutryn TPs help to
563 identify degradation pathways, distinct degradation pathways may lead to the same TPs,
564 thereby limiting the interpretation. Our results highlight that terbutryn CSIA can help
565 identifying underlying degradation pathways based on a dual isotope approach and
566 differentiate pathways *in situ*, even without TP measurements. Isotope fractionation patterns
567 during direct and indirect terbutryn photodegradation under simulated sunlight are similar,
568 while terbutryn biodegradation does not lead to significant isotope fractionation. Hence,
569 carbon and nitrogen stable isotope fractionation may help to distinguish terbutryn
570 photodegradation from biodegradation in environmental studies.

571 In the future, insights into degradation pathways from ME-CSIA may be gained with
572 sulphur stable isotope fractionation ($\delta^{34}\text{S}$) during terbutryn degradation based on GC-MS-
573 ICPMS measurements (Kümmel et al., 2020; Torrentó et al., 2021). Sulphur stable isotope
574 values may significantly change during biodegradation through the formation of TerSO, while
575 the formation of a bond between the sulphur and oxygen atoms may cause an inverse isotope
576 effect (i.e., more negative $\delta^{34}\text{S}$ values) (Figure 4). It is thus expected that sulphur stable
577 isotope fractionation may help teasing apart biodegradation and photodegradation during
578 terbutryn leaching from the facade up to groundwater.

579 Altogether, we anticipate our study to be a starting point for a new strategy including
580 ME-CSIA to examine terbutryn transformation on facades and in receiving environmental
581 compartments to follow up mitigation measures to limit biocide release.

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Author contribution statement

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

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References

- Alvarez-Zaldívar, P., Payraudeau, S., Meite, F., Masbou, J., Imfeld, G., 2018. Pesticide degradation and export losses at the catchment scale: insights from compound-specific isotope analysis (CSIA). *Water Res.* 139, 198–207. <https://doi.org/10.1016/j.watres.2018.03.061>
- Austnes, K., Aherne, J., Arle, J., Čičendajeva, M., Couture, S., Fölster, J., Garmo, Ø.A., Hruska, J., Monteith, D., Posch, M., Rogora, M., Sample, J.E., Skjelkvåle, B.L., Steingruber, S., Stoddard, J.L., Ulańczyk, R., Van Dam, H., Velasco, M.T., Vuorenmaa, J., Wright, R.F., de Wit, H., 2018. Regional assessment of the current extent of acidification of surface waters in Europe and North America, 134. Norwegian institute for water research.
- Bollmann, U.E., Fernández-Calviño, D., Brandt, K.K., Storgaard, M.S., Sanderson, H., Bester, K., 2017a. Biocide runoff from building facades: degradation kinetics in soil. *Environ. Sci. Technol.* 51, 3694–3702. <https://doi.org/10.1021/acs.est.6b05512>
- Bollmann, U.E., Minelgaite, G., Schlüsener, M., Ternes, T., Vollertsen, J., Bester, K., 2016. Leaching of terbutryn and its photodegradation products from artificial walls under natural weather conditions. *Environ. Sci. Technol.* 50, 4289–4295. <https://doi.org/10.1021/acs.est.5b05825>
- Bollmann, U.E., Minelgaite, G., Schlüsener, M., Ternes, T.A., Vollertsen, J., Bester, K., 2017b. Photodegradation of octylisothiazolinone and semi-field emissions from facade coatings. *Sci. Rep.* 7, 41501. <https://doi.org/10.1038/srep41501>
- Burkhardt, M., Junghans, M., Zuleeg, S., Boller, M., Schoknecht, U., Lamani, X., Bester, K., Vonbank, R., Simmler, H., 2009. Biozide in Gebäudefassaden – ökotoxikologische Effekte, Auswaschung und Belastungsabschätzung für Gewässer. *Environ. Sci. Eur.* 21, 36–47. <https://doi.org/10.1007/s12302-008-0033-1>

630 Burkhardt, M., Zuleeg, S., Vonbank, R., Bester, K., Carmeliet, J., Boller, M., Wangler, T., 2012.
631 Leaching of biocides from façades under natural weather conditions. *Environ. Sci. Technol.* 46,
632 5497–5503. <https://doi.org/10.1021/es2040009>

633 Burrows, H.D., Canle L, M., Santaballa, J.A., Steenken, S., 2002. Reaction pathways and mechanisms
634 of photodegradation of pesticides. *J. Photochem. Photobiol. B: Biol.* 67, 71–108.
635 [https://doi.org/10.1016/S1011-1344\(02\)00277-4](https://doi.org/10.1016/S1011-1344(02)00277-4)

636 Carazo-Rojas, E., Pérez-Rojas, G., Pérez-Villanueva, M., Chinchilla-Soto, C., Chin-Pampillo, J.S., Aguilar-
637 Mora, P., Alpízar-Marín, M., Masís-Mora, M., Rodríguez-Rodríguez, C.E., Vryzas, Z., 2018. Pesticide
638 monitoring and ecotoxicological risk assessment in surface water bodies and sediments of a
639 tropical agro-ecosystem. *Environ. Pollut.* 241, 800–809.
640 <https://doi.org/10.1016/j.envpol.2018.06.020>

641 Ccancapa, A., Masiá, A., Navarro-Ortega, A., Picó, Y., Barceló, D., 2016. Pesticides in the Ebro river
642 basin: occurrence and risk assessment. *Environ. Pollut.* 211, 414–424.
643 <https://doi.org/10.1016/j.envpol.2015.12.059>

644 CIE, 1989. CIE 85 - Solar Spectral Irradiance (1st Edition) (E) | Engineering360, International
645 Comission on Illumination (CIE).

646 Comber, S.D.W., 1999. Abiotic persistence of atrazine and simazine in water. *Pesticide Science* 55,
647 696–702. [https://doi.org/10.1002/\(SICI\)1096-9063\(199907\)55:7<696::AID-PS11>3.0.CO;2-7](https://doi.org/10.1002/(SICI)1096-9063(199907)55:7<696::AID-PS11>3.0.CO;2-7)

648 Coplen, T.B., 2011. Guidelines and recommended terms for expression of stable-isotope-ratio and
649 gas-ratio measurement results. *Rapid Commun. Mass Spectrom.* 25, 2538–2560.
650 <https://doi.org/10.1002/rcm.5129>

651 Drouin, G., Droz, B., Leresche, F., Payraudeau, S., Masbou, J., Imfeld, G., 2021. Direct and indirect
652 photodegradation of atrazine and S-metolachlor in agriculturally impacted surface water and
653 associated C and N isotope fractionation. *Environ. Sci.: Processes Impacts* 23, 1791–1802.
654 <https://doi.org/10.1039/D1EM00246E>

655 Droz, B., Drouin, G., Maurer, L., Villette, C., Payraudeau, S., Imfeld, G., 2021. Phase transfer and
656 biodegradation of pesticides in water–sediment systems explored by compound-specific isotope
657 analysis and conceptual modeling. *Environ. Sci. Technol.* 55, 4720–4728.
658 <https://doi.org/10.1021/acs.est.0c06283>

659 Elsner, M., 2010. Stable isotope fractionation to investigate natural transformation mechanisms of
660 organic contaminants: principles, prospects and limitations. *J. Environ. Monit.* 12, 2005–2031.
661 <https://doi.org/10.1039/COEM00277A>

662 Elsner, M., Imfeld, G., 2016. Compound-specific isotope analysis (CSIA) of micropollutants in the
663 environment — current developments and future challenges. *Curr. Opin. Biotechnol., Analytical*
664 *biotechnology* 41, 60–72. <https://doi.org/10.1016/j.copbio.2016.04.014>

665 Elsner, M., Jochmann, M.A., Hofstetter, T.B., Hunkeler, D., Bernstein, A., Schmidt, T.C.,
666 Schimmelfmann, A., 2012. Current challenges in compound-specific stable isotope analysis of
667 environmental organic contaminants. *Anal. Bioanal. Chem.* 403, 2471–2491.
668 <https://doi.org/10.1007/s00216-011-5683-y>

669 European Council Directive 91/414/EEC, 2002. Commission Regulation (EC) No 2076/2002 of 20
670 November 2002 extending the time period referred to in Article 8(2) of Council Directive
671 91/414/EEC and concerning the non-inclusion of certain active substances in Annex I to that
672 Directive and the withdrawal of authorisations for plant protection products containing these
673 substances (Text with EEA relevance), OJ L.

674 European Council Directive 2013/39/EU, 2013. Directive 2013/39/EU of the European Parliament and
675 of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards
676 priority substances in the field of water policy Text with EEA relevance, OJ L.

677 Fenner, K., Canonica, S., Wackett, L.P., Elsner, M., 2013. Evaluating pesticide degradation in the
678 environment: blind spots and emerging opportunities. *Science*.
679 <https://doi.org/10.1126/science.1236281>

680 Fischer, A., Manefield, M., Bombach, P., 2016. Application of stable isotope tools for evaluating
681 natural and stimulated biodegradation of organic pollutants in field studies. *Curr. Opin.*
682 *Biotechnol.* 41, 99–107. <https://doi.org/10.1016/j.copbio.2016.04.026>

683 Grant, W.D., Sorokin, D.Yu., 2011. Distribution and diversity of soda lake alkaliphiles, in: Horikoshi, K.
684 (Ed.), *Extremophiles Handbook*. Springer Japan, Tokyo, pp. 27–54. [https://doi.org/10.1007/978-4-](https://doi.org/10.1007/978-4-431-53898-1_3)
685 [431-53898-1_3](https://doi.org/10.1007/978-4-431-53898-1_3)

686 Harada, N., Takagi, K., Fujii, K., Iwasaki, A., 2006. Transformation of methylthio-s-triazines via sulfur
687 oxidation by strain JUN7, a *Bacillus cereus* species. *Soil Biol. Biochem.* 38, 2952–2957.
688 <https://doi.org/10.1016/j.soilbio.2006.03.018>

689 Hartenbach, A.E., Hofstetter, T.B., Tentscher, P.R., Canonica, S., Berg, M., Schwarzenbach, R.P., 2008.
690 Carbon, hydrogen, and nitrogen isotope fractionation during light-induced transformations of
691 atrazine. *Environ. Sci. Technol.* 42, 7751–7756. <https://doi.org/10.1021/es800356h>

692 Hensen, B., Lange, J., Jackisch, N., Zieger, F., Olsson, O., Kümmerer, K., 2018. Entry of biocides and
693 their transformation products into groundwater via urban stormwater infiltration systems. *Water*
694 *Res.* 144, 413–423. <https://doi.org/10.1016/j.watres.2018.07.046>

695 Hensen, B., Olsson, O., Kümmerer, K., 2019. The role of irradiation source setups and indirect
696 phototransformation: kinetic aspects and the formation of transformation products of weakly
697 sunlight-absorbing pesticides. *Sci. Total Environ.* 695, 133808.
698 <https://doi.org/10.1016/j.scitotenv.2019.133808>

699 Hoefs, J., 2015. *Stable isotope geochemistry*. Springer International Publishing, Cham.
700 <https://doi.org/10.1007/978-3-319-19716-6>

701 Höhener, P., Imfeld, G., 2021. Quantification of Lambda (λ) in multi-elemental compound-specific
702 isotope analysis. *Chemosphere* 267. <https://doi.org/10.1016/j.chemosphere.2020.129232>

703 Höhener, P., Yu, X., 2012. Stable carbon and hydrogen isotope fractionation of dissolved organic
704 groundwater pollutants by equilibrium sorption. *J. Contam. Hydrol.* 129–130, 54–61.
705 <https://doi.org/10.1016/j.jconhyd.2011.09.006>

706 Ivdra, N., Herrero-Martín, S., Fischer, A., 2014. Validation of user- and environmentally friendly
707 extraction and clean-up methods for compound-specific stable carbon isotope analysis of
708 organochlorine pesticides and their metabolites in soils. *J. Chromatogr. A* 1355, 36–45.
709 <https://doi.org/10.1016/j.chroma.2014.06.014>

710 Jungnickel, C., Stock, F., Brandsch, T., Ranke, J., 2008. Risk assessment of biocides in roof paint. Part
711 1: experimental determination and modelling of biocide leaching from roof paint. *Environ. Sci.*
712 *Pollut. Res. Int.* 15, 258–265. <https://doi.org/10.1065/espr2007.12.465>

713 Jurado, A., Fernandes, M., Videira, R., Peixoto, F., Vicente, J., 2011. Herbicides: the face and the
714 reverse of the coin. An in vitro approach to the toxicity of herbicides in non-target organisms,
715 *Herbicides and Environment*. IntechOpen. <https://doi.org/10.5772/12976>

716 Kaufman, D.D., Kearney, P.C., 1976. Microbial transformations in the soil. *Herbicides: Physiology*.

717 Keresztesi, Á., Birsan, M.-V., Nita, I.-A., Bodor, Z., Szép, R., 2019. Assessing the neutralisation, wet
718 deposition and source contributions of the precipitation chemistry over Europe during 2000–
719 2017. *Environ. Sci. Eur.* 31, 50. <https://doi.org/10.1186/s12302-019-0234-9>

720 Knossow, N., Siebner, H., Bernstein, A., 2020. Isotope analysis method for the herbicide bromoxynil
721 and its application to study photo-degradation processes. *J. Hazard. Mater.* 388, 122036.
722 <https://doi.org/10.1016/j.jhazmat.2020.122036>

723 Kresmann, S., Arokia, A.H.R., Koch, C., Sures, B., 2018. Ecotoxicological potential of the biocides
724 terbutryn, octhiline and methylisothiazolinone: underestimated risk from biocidal pathways?
725 *Sci. Total Environ.* 625, 900–908. <https://doi.org/10.1016/j.scitotenv.2017.12.280>

726 Kümmel, S., Horst, A., Gelman, F., Strauss, H., Richnow, H.H., Gehre, M., 2020. Simultaneous
727 compound-specific analysis of $\delta^{33}\text{S}$ and $\delta^{34}\text{S}$ in organic compounds by GC-MC-ICPMS using
728 medium- and low-mass-resolution modes. *Anal. Chem.* 92, 14685–14692.
729 <https://doi.org/10.1021/acs.analchem.0c03253>

730 Lam, M.W., Tantuco, K., Mabury, S.A., 2003. PhotoFate: a new approach in accounting for the
731 contribution of indirect photolysis of pesticides and pharmaceuticals in surface waters. *Environ.*
732 *Sci. Technol.* 37, 899–907. <https://doi.org/10.1021/es025902+>

733 Le, T.D.H., Scharmüller, A., Kattwinkel, M., Kühne, R., Schüürmann, G., Schäfer, R.B., 2017.
734 Contribution of waste water treatment plants to pesticide toxicity in agriculture catchments.
735 *Ecotoxicol. Environ. Saf.* 145, 135–141. <https://doi.org/10.1016/j.ecoenv.2017.07.027>

736 LeBaron, H.M., McFarland, J.E., Burnside, O., 2008. The triazine herbicides: 50 years revolutionizing
737 agriculture. Elsevier.

738 Lechón, Y., Sánchez-Brunete, C., Tadeo, J.L., 1997. Influence of the laboratory incubation method on
739 chlorotoluron and terbutryn degradation in soil. *J. Agric. Food Chem.* 45, 951–954.
740 <https://doi.org/10.1021/jf960340x>

741 Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk
742 assessments and management. *Hum. Ecol. Risk Assess.* 22, 1050–1064.
743 <https://doi.org/10.1080/10807039.2015.1133242>

744 Lihl, C., Heckel, B., Grzybkowska, A., Dybala-Defratyka, A., Ponsin, V., Torrentó, C., Hunkeler, D.,
745 Elsner, M., 2020. Compound-specific chlorine isotope fractionation in biodegradation of atrazine.
746 *Environ. Sci.: Processes Impacts* 22, 792–801. <https://doi.org/10.1039/C9EM00503J>

747 Linke, F., Olsson, O., Preusser, F., Kümmerer, K., Schnarr, L., Bork, M., Lange, J., 2021. Sources and
748 pathways of biocides and their transformation products in urban storm water infrastructure of a 2
749 ha urban district. *Hydrol. Earth Syst. Sci.* 25, 4495–4512. [https://doi.org/10.5194/hess-25-4495-](https://doi.org/10.5194/hess-25-4495-2021)
750 2021

751 Luft, A., Wagner, M., Ternes, T.A., 2014. Transformation of biocides irgarol and terbutryn in the
752 biological wastewater treatment. *Environ. Sci. Technol.* 48, 244–254.
753 <https://doi.org/10.1021/es403531d>

754 Mabey, W., Mill, T., 1978. Critical review of hydrolysis of organic compounds in water under
755 environmental conditions. *J. Phys. Chem. Ref. Data* 7, 383–415. <https://doi.org/10.1063/1.555572>

756 Machate, O., Dellen, J., Schulze, T., Wentzky, V.C., Krauss, M., Brack, W., 2021. Evidence for
757 antifouling biocides as one of the limiting factors for the recovery of macrophyte communities in
758 lakes of Schleswig-Holstein. *Environ. Sci. Eur.* 33, 57. <https://doi.org/10.1186/s12302-021-00500-3>

759 Masbou, J., Drouin, G., Payraudeau, S., Imfeld, G., 2018. Carbon and nitrogen stable isotope
760 fractionation during abiotic hydrolysis of pesticides. *Chemosphere* 213, 368–376.
761 <https://doi.org/10.1016/j.chemosphere.2018.09.056>

762 Meyer, A.H., Penning, H., Elsner, M., 2009. C and N isotope fractionation suggests similar
763 mechanisms of microbial atrazine transformation despite involvement of different enzymes (AtzA
764 and TrzN). *Environ. Sci. Technol.* 43, 8079–8085. <https://doi.org/10.1021/es9013618>

765 Minelgaite, G., Nielsen, A.H., Pedersen, M.L., Vollertsen, J., 2017. Photodegradation of three
766 stormwater biocides. *Urban Water J.* 14, 53–60. <https://doi.org/10.1080/1573062X.2015.1076489>

767 Muir, D.C., Yarechewski, A.L., 1982. Degradation of terbutryn in sediments and water under various
768 redox conditions. *J. Environ. Sci. Health - B Pestic. Food Contam. Agric. Wastes* 17, 363–380.
769 <https://doi.org/10.1080/03601238209372327>

770 Ojeda, A.S., Phillips, E., Mancini, S.A., Lollar, B.S., 2019. Sources of uncertainty in biotransformation
771 mechanistic interpretations and remediation studies using CSIA. *Anal. Chem.* 91, 9147–9153.
772 <https://doi.org/10.1021/acs.analchem.9b01756>

773 Paijens, C., Bressy, A., Frère, B., Tedoldi, D., Mailler, R., Rocher, V., Neveu, P., Moilleron, R., 2021.
774 Urban pathways of biocides towards surface waters during dry and wet weathers: assessment at
775 the Paris conurbation scale. *J. Hazard. Mater.* 402, 123765.
776 <https://doi.org/10.1016/j.jhazmat.2020.123765>

777 Pfeifroth, U., Sanchez-Lorenzo, A., Manara, V., Trentmann, J., Hollmann, R., 2018. Trends and
778 variability of surface solar radiation in Europe based on surface- and satellite-based data records.
779 *J. Geophys. Res. Atmos.* 123, 1735–1754. <https://doi.org/10.1002/2017JD027418>

780 Poursat, B.A.J., van Spanning, R.J.M., de Voogt, P., Parsons, J.R., 2019. Implications of microbial
781 adaptation for the assessment of environmental persistence of chemicals. *Crit. Rev. Environ. Sci.*
782 *Technol.* 49, 2220–2255. <https://doi.org/10.1080/10643389.2019.1607687>

783 QSun/QLab, 2011. Q-Lab QSun Technical bulletin LU-0822: sunlight, weathering & light stability
784 testing [WWW Document]. URL [https://www.q-lab.com/documents/public/cd131122-c252-4142-](https://www.q-lab.com/documents/public/cd131122-c252-4142-86ce-5ba366a12759.pdf)
785 [86ce-5ba366a12759.pdf](https://www.q-lab.com/documents/public/cd131122-c252-4142-86ce-5ba366a12759.pdf) (accessed 2.9.22).

786 Quednow, K., Püttmann, W., 2007. Monitoring terbutryn pollution in small rivers of Hesse, Germany.
787 *J. Environ. Monit.* 9, 1337–1343. <https://doi.org/10.1039/B711854F>

788 Russell, J.D., Cruz, M., White, J.L., Bailey, G.W., W. R. Payne, J., J. D. Pope, J., Teasley, J.I., 1968. Mode
789 of chemical degradation of s-triazines by montmorillonite. *Science*.
790 <https://doi.org/10.1126/science.160.3834.1340>

791 Sakkas, V.A., Konstantinou, I.K., Albanis, T.A., 2006. Photochemical fate of organic booster biocides in
792 the aquatic environment, in: Konstantinou, I.K. (Ed.), *Antifouling Paint Biocides, The Handbook of*
793 *Environmental Chemistry*. Springer, Berlin, Heidelberg, pp. 171–200.
794 https://doi.org/10.1007/698_5_054

795 Schmidt, T.C., Zwank, L., Elsner, M., Berg, M., Meckenstock, R.U., Haderlein, S.B., 2004. Compound-
796 specific stable isotope analysis of organic contaminants in natural environments: a critical review
797 of the state of the art, prospects, and future challenges. *Anal. Bioanal. Chem.* 378, 283–300.
798 <https://doi.org/10.1007/s00216-003-2350-y>

799 Schoknecht, U., Gruycheva, J., Mathies, H., Bergmann, H., Burkhardt, M., 2009. Leaching of biocides
800 used in façade coatings under laboratory test conditions. *Environ. Sci. Technol.* 43, 9321–9328.
801 <https://doi.org/10.1021/es9019832>

802 Schoknecht, U., Mathies, H., Lisec, J., 2021. Leaching and transformation of film preservatives in
803 paints induced by combined exposure to ultraviolet radiation and water contact under controlled
804 laboratory conditions. *Water* 13, 2390. <https://doi.org/10.3390/w13172390>

805 Schürner, H.K.V., Seffernick, J.L., Grzybkowska, A., Dybala-Defratyka, A., Wackett, L.P., Elsner, M.,
806 2015. Characteristic isotope fractionation patterns in s-triazine degradation have their origin in
807 multiple protonation options in the s-triazine hydrolase TrzN. *Environ. Sci. Technol.* 49, 3490–
808 3498. <https://doi.org/10.1021/es5055385>

809 Schüth, C., Taubald, H., Bolaño, N., Maciejczyk, K., 2003. Carbon and hydrogen isotope effects during
810 sorption of organic contaminants on carbonaceous materials. *J. Contam. Hydrol.* 64, 269–281.
811 [https://doi.org/10.1016/S0169-7722\(02\)00216-4](https://doi.org/10.1016/S0169-7722(02)00216-4)

812 Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 2005. *Environmental organic chemistry*. John
813 Wiley & Sons.

814 Scott, K.M., Lu, X., Cavanaugh, C.M., Liu, J.S., 2004. Optimal methods for estimating kinetic isotope
815 effects from different forms of the Rayleigh distillation equation. *Geochim. Cosmochim. Acta* 68,
816 433–442. [https://doi.org/10.1016/S0016-7037\(03\)00459-9](https://doi.org/10.1016/S0016-7037(03)00459-9)

817 Spain, J.C., Pritchard, P.H., Bourquin, A.W., 1980. Effects of adaptation on biodegradation rates in
818 sediment/water cores from estuarine and freshwater environments. *Appl. Environ. Microbiol.* 40,
819 726–734. <https://doi.org/10.1128/aem.40.4.726-734.1980>

820 Styszko, K., Bollmann, U.E., Bester, K., 2015. Leaching of biocides from polymer renders under
821 wet/dry cycles--rates and mechanisms. *Chemosphere* 138, 609–615.
822 <https://doi.org/10.1016/j.chemosphere.2015.07.029>

823 Styszko, K., Bollmann, U.E., Wangler, T.P., Bester, K., 2014. Desorption of biocides from renders
824 modified with acrylate and silicone. *Chemosphere* 95, 188–192.
825 <https://doi.org/10.1016/j.chemosphere.2013.08.064>

826 Talja, K.M., Kaukonen, S., Kilpi-Koski, J., Malin, I., Kairesalo, T., Romantschuk, M., Tuominen, J.,
827 Kontro, M.H., 2008. Atrazine and terbutryn degradation in deposits from groundwater
828 environment within the boreal region in Lahti, Finland. *J. Agric. Food Chem.* 56, 11962–11968.
829 <https://doi.org/10.1021/jf802528a>

830 Torabi, E., Wiegert, C., Guyot, B., Vuilleumier, S., Imfeld, G., 2020. Dissipation of S-metolachlor and
831 butachlor in agricultural soils and responses of bacterial communities: insights from compound-
832 specific isotope and biomolecular analyses. *J. Environ. Sci.* 92, 163–175.
833 <https://doi.org/10.1016/j.jes.2020.02.009>

834 Torrentó, C., Ponsin, V., Lihl, C., Hofstetter, T.B., Baran, N., Elsner, M., Hunkeler, D., 2021. Triple-
835 element compound-specific stable isotope analysis (3D-CSIA): added value of Cl isotope ratios to
836 assess herbicide degradation. *Environ. Sci. Technol.* 55, 13891–13901.
837 <https://doi.org/10.1021/acs.est.1c03981>

838 Urbanczyk, M.M., Bester, K., Borho, N., Schoknecht, U., Bollmann, U.E., 2019. Influence of pigments
839 on phototransformation of biocides in paints. *J. Hazard. Mater.* 364, 125–133.
840 <https://doi.org/10.1016/j.jhazmat.2018.10.018>

841 Verlicchi, P., Al Aukidy, M., Zambello, E., 2012. Occurrence of pharmaceutical compounds in urban
842 wastewater: removal, mass load and environmental risk after a secondary treatment—a review.
843 *Sci. Total Environ.* 429, 123–155. <https://doi.org/10.1016/j.scitotenv.2012.04.028>

844 Vermeesch, P., 2018. IsoplotR: a free and open toolbox for geochronology. *Geosci. Front.* 9, 1479–
845 1493. <https://doi.org/10.1016/j.gsf.2018.04.001>

846 Wittmer, I.K., Scheidegger, R., Bader, H.-P., Singer, H., Stamm, C., 2011. Loss rates of urban biocides
847 can exceed those of agricultural pesticides. *Sci. Total Environ.* 409, 920–932.
848 <https://doi.org/10.1016/j.scitotenv.2010.11.031>

849 Wolfe, N.L., Mingelgrin, U., Miller, G.C., 1990. Abiotic transformations in water, sediments, and soil,
850 in: *Pesticides in the Soil Environment: Processes, Impacts and Modeling*. John Wiley & Sons, Ltd,
851 pp. 103–168. <https://doi.org/10.2136/sssabookser2.c5>

852 Wu, B., Arnold, W.A., Ma, L., 2021. Photolysis of atrazine: role of triplet dissolved organic matter and
853 limitations of sensitizers and quenchers. *Water Research* 190, 116659.
854 <https://doi.org/10.1016/j.watres.2020.116659>

855 Yang, W., Zhou, H., Cicek, N., 2014. Treatment of organic micropollutants in water and wastewater by
856 UV-based processes: a literature review. *Crit. Rev. Environ. Sci. Technol.* 44, 1443–1476.
857 <https://doi.org/10.1080/10643389.2013.790745>

858 Zhang, N., Schindelka, J., Herrmann, H., George, C., Rosell, M., Herrero-Martín, S., Klán, P., Richnow,
859 H.H., 2015. Investigation of humic substance photosensitized reactions via carbon and hydrogen
860 isotope fractionation. *Environ. Sci. Technol.* 49, 233–242. <https://doi.org/10.1021/es502791f>

861