

1 **Short-term facilitation of microbial litter decomposition by ultraviolet radiation**

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14 **Abstract**

15 Solar radiation plays an important role in carbon cycling by increasing the decomposition rates of  
16 plant litter and soil organic matter (i.e. photodegradation). Previous work suggests that exposure  
17 to radiation can facilitate microbial decomposition of litter by altering litter chemistry and  
18 consequently litter degradability (i.e. photopriming). However, it remains unclear to what extent  
19 photopriming contributes to litter decomposition processes and on what timescale photopriming  
20 operates. We conducted laboratory experiments to compare the effects of UV photopriming at  
21 two temporal scales (months versus days). In one experiment, we found that four months of UV  
22 exposure induced a significant but small (3-4%) mass loss in two of three litter species commonly  
23 found in California oak savanna; however, UV exposure did not alter litter degradability as  
24 measured by microbial respiration in an incubation experiment. We also found that UV exposure  
25 had limited effects on lignin and other cell wall structures, but one month of microbial  
26 decomposition (in absence of UV exposure) significantly reduced lignin  $\beta$ -aryl ether inter-unit  
27 linkages and acetylated xylans. These results indicate that abiotic photodegradation alone was  
28 ineffective at breaking down lignin. In another experiment, litter of a common grass was exposed  
29 to either alternating UV radiation and dark conditions, or constant darkness for 128 days. We  
30 found that the alternating UV exposure increased litter CO<sub>2</sub> production in both dark and UV  
31 phases over that observed in constant darkness. This led to a 35% greater release of CO<sub>2</sub> from the  
32 alternating UV exposure treatment between days 65 and 128 of the experiment. These results  
33 demonstrate that alternating UV exposure with dark conditions is key to enabling photopriming  
34 on a timescale of days. Overall, we identify short-term photopriming as a novel mechanism  
35 behind photodegradation. Our results also challenge the conventional hypothesis that abiotic  
36 processes are primarily responsible for degrading lignin during photodegradation.

37

38 **Keywords**

39 Photo-oxidation; photodegradation; cellulose; hemicellulose; NMR (nuclear magnetic resonance);

40 HSQC (heteronuclear single-quantum coherence)

41

## 42 **1. Introduction**

43 There are large uncertainties in current predictions of how the terrestrial carbon (C) cycle will  
44 respond to future climatic changes (Smith et al., 2013; Carvalhais et al., 2014; Smith et al., 2016).  
45 A major source of uncertainty is the difficulty in quantifying ecosystem C fluxes and attributing  
46 their variations among abiotic and biotic controls (Lombardozzi et al., 2015; Wieder et al., 2015).  
47 Litter decomposition is the central ecosystem process that transfers C from a transient pool in  
48 vegetation to a stabilized pool in soil (Berg and McClaugherty, 2008). Conventional theories of  
49 litter decomposition focus on understanding the environmental and chemical controls of biotic  
50 decomposition (Melillo et al., 1982; Coūteaux et al., 1995). Empirical models developed based on  
51 these theories are successful overall, but they systematically underestimate litter decomposition  
52 rates in many arid and semi-arid environments (Schaefer et al., 1985; Parton et al., 2007; Adair et  
53 al., 2008). This knowledge gap has sparked a new and growing field of research on  
54 photodegradation (Austin and Vivanco, 2006; King et al., 2012; Song et al., 2013; Liu et al.,  
55 2014; Barnes et al., 2015). Here, the term “photodegradation” refers to the combination of abiotic  
56 and biotic effects of solar radiation on decomposition processes.

57 Abiotic photodegradation refers to the photochemical and/or thermal mineralization of organic  
58 matter upon exposure to solar radiation, including ultraviolet (UV; 280-400 nm) and  
59 photosynthetically active radiation (PAR; 400-700 nm) (Brandt et al., 2009; Lee et al., 2012;  
60 Whelan and Rhew, 2014). Laboratory studies have linked abiotic photodegradation processes to  
61 the breakdown of litter and soil organic matter and emissions of CO, CO<sub>2</sub>, CH<sub>4</sub>, and volatile  
62 organic compounds (Schade et al., 1999; Leff and Fierer, 2008; Brandt et al., 2009). These abiotic  
63 emissions of trace gases are typically small in magnitude (reviewed by King et al., 2012), making  
64 it difficult to directly measure them in the field (van Asperen et al., 2015). The litter mass loss  
65 induced by abiotic photodegradation is also generally small (reviewed by Song et al., 2013; Wang  
66 et al., 2015) compared to the results from field studies showing that exposure to solar radiation

67 increased mass loss by 25% to 60% (Austin and Vivanco, 2006; Brandt et al., 2010; Huang et al.,  
68 2017).

69 Photodegradation can also contribute to litter mass loss by facilitating microbial  
70 decomposition, a process known as photopriming (Barnes et al., 2015). Photopriming has often  
71 been included as a key component of photodegradation (e.g., Day et al., 2007; Gallo et al., 2009).  
72 More recent studies have begun to isolate and quantify the specific contribution of photopriming  
73 to litter decomposition (Foereid et al., 2010; Lin et al., 2015b; Wang et al., 2015; Yanni et al.,  
74 2015; Austin et al., 2016). It is hypothesized that photopriming is enabled via abiotic  
75 photodegradation of lignin, a main component of the plant cell wall that usually impedes  
76 microbial decomposition (King et al., 2012; Baker and Allison, 2015). Degradation of lignin  
77 allows microbial decomposers to access other litter substrates, thus increasing microbial litter  
78 decomposition. Many studies support this mechanism and report radiation-induced decreases in  
79 litter lignin content and increases in litter degradability during microbial decomposition (Henry et  
80 al., 2008; Austin and Ballaré, 2010; Frouz et al., 2011; Wang et al., 2015; Austin et al., 2016).  
81 However, it is unclear whether the loss of lignin was caused solely by abiotic photodegradation or  
82 a combination of abiotic photodegradation and photopriming of microbial decomposition. In  
83 addition, a large number of studies did not find facilitation effects of radiation exposure on litter  
84 degradability, further questioning the prevalence of photopriming (Brandt et al., 2009;  
85 Kirschbaum et al., 2011; Lambie et al., 2014; Lin et al., 2015b).

86 Identifying the underlying mechanisms of photopriming would help to resolve the above  
87 contradicting results of photopriming research. Past photopriming studies usually separated  
88 radiation treatment and the assessment of litter degradability into two consecutive phases. The  
89 first phase, radiation treatment, typically lasted for several months to a year and was often  
90 implemented under field or greenhouse conditions (Henry et al., 2008; Lin et al., 2015b; Wang et  
91 al., 2015; Austin et al., 2016). The second phase, assessment of litter degradability, was generally

92 conducted without radiation manipulation under controlled field or laboratory conditions (Brandt  
93 et al., 2009; Lambie et al., 2014; Yanni et al., 2015; Austin et al., 2016). However, under natural  
94 conditions, litter experiences abiotic photodegradation and microbial decomposition  
95 simultaneously on a daily basis. Gliksman et al. (2016) recently demonstrated that daytime  
96 photodegradation primed litter microbial decomposition at night in a Mediterranean ecosystem,  
97 suggesting photoprimering can occur at a diel scale. Therefore, photoprimering might have occurred  
98 but was undetected during the first phase of a two-phase experiment. The two-phase design is  
99 thus likely to underestimate or misrepresent the contribution of photoprimering to litter  
100 decomposition in the field. A comparison of the photoprimering effects at different temporal scales  
101 (e.g. seasonal vs. daily) is currently lacking and would improve our understanding of the role of  
102 photoprimering in litter decomposition processes.

103 Unlike the studies mentioned above, a number of other studies did not find preferential  
104 breakdown of lignin by photodegradation (Brandt et al., 2007; Lin and King, 2014; Baker and  
105 Allison, 2015), highlighting the lack of understanding of the underlying chemical mechanism  
106 behind photodegradation. Most previous studies relied on proximate analyses that sequentially  
107 extracted litter with solvents and assumed the acid-unhydrolyzable residues to be lignin. This  
108 assumption is strongly challenged in the field of decomposition science (Sluiter et al., 2010;  
109 Preston and Trofymow, 2015), which has led to several recent studies that examined changes in  
110 lignin chemical composition during photodegradation (Feng et al., 2011; Frouz et al., 2011). For  
111 instance, using two-dimensional nuclear magnetic resonance (2D NMR) spectroscopic  
112 techniques, we found that field UV radiation exposure degraded lignin  $\beta$ -aryl ether units and  
113 hemicelluloses (Lin et al., 2015a). In the current literature, however, there is no consistent pattern  
114 to describe how photodegradation alters lignin chemistry. It is also unclear whether abiotic  
115 photodegradation and microbial decomposition target similar lignin structures.

116 Here we present results from two controlled laboratory experiments that examine the  
117 mechanisms of photopriming at two different temporal scales. In the first experiment (*two-phase*  
118 *photopriming*), we exposed three types of litter to UV radiation for four months in the laboratory  
119 and evaluated the effects of abiotic photodegradation induced by UV radiation (hereafter, abiotic  
120 UV photodegradation) on litter mass loss and litter degradability. We also compared the effects of  
121 abiotic UV photodegradation and microbial decomposition on litter cell wall chemistry using 2D  
122 NMR techniques. In the second experiment (*short-term photopriming*), a grass litter was exposed  
123 to either alternating UV radiation and dark conditions or kept continuously in darkness in order to  
124 assess photopriming on a daily temporal scale. We hypothesized that 1) an extended period of UV  
125 exposure would stimulate litter mass loss due to abiotic photodegradation and increase litter  
126 biodegradability as a result of UV-induced lignin degradation; 2) abiotic UV photodegradation  
127 would be more effective in altering lignin chemistry compared to microbial decomposition; and  
128 3) microbial decomposition of litter would be enhanced under an alternating light regime  
129 compared to continuous darkness as a result of short-term photopriming.

130

## 131 **2. Materials and Methods**

### 132 2.1. Study site and sample collection

133 Litter and soil samples were collected from the University of California's Sedgwick Reserve  
134 in Santa Ynez, CA, USA (34°42'N, 120°2'W), where the mean elevation is approximately 400  
135 m.a.s.l., the mean annual precipitation is 380 mm, and the mean annual temperature is 16.8 °C.  
136 The study site features a Mediterranean climate with hot, dry summers and cool, wet winters.  
137 Vegetation is characteristic of a California oak savanna that is dominated by several invasive  
138 annual grass species: *Bromus diandrus*, *Avena fatua*, and *Bromus hordeaceus*. Several oak  
139 species, including blue oak (*Quercus douglasii*), coast live oak (*Quercus agrifolia*), and valley

140 oak (*Quercus lobata*), are widely spaced in the grassland matrix. Soil is classified as Haploxerolls  
141 with high clay concentrations.

142 Standing dead, senesced litter from *B. diandrus* and *A. fatua* was harvested in July 2013 after  
143 the end of the growing season. Recently fallen leaves of *Q. douglasii* were also collected. Upon  
144 return to the laboratory, *B. diandrus* and *A. fatua* litter was cut into pieces of approximately 10  
145 cm in length. All litter samples were oven-dried at 60 °C for two days and then stored in the dark  
146 at room temperature until used in the two experiments described here.

## 147 2.2. Two-phase photoprimering experiment

148 *Radiation exposure.* The experiment follows a factorial design of litter type (*A. fatua*, *B.*  
149 *diandrus*, and *Q. douglasii*) and UV manipulation (UV exposure and control) with three  
150 replicates. Oven-dried litter was enclosed in custom-built envelopes that were made of UV-  
151 transparent polychlorotrifluoroethylene film (0.0635 mm thickness, HydroBlock GP2500,  
152 Honeywell International Inc., Morris Plains, NJ) and sealed on the edges with vinyl tape. This  
153 film is optically equivalent to Aclar film (Day et al., 2007; Uselman et al., 2011) and transmits  
154 over 94% of radiation in the UV range. By flipping the envelopes every week, both sides of the  
155 samples were exposed to UV radiation. Envelopes also helped to reduce overlapping of litter.  
156 Note that the envelopes were not air-tight. Eighteen envelopes were constructed. A set of three  
157 envelopes, each with one litter type, was placed 10 cm under four UV lamps (UVB-313EL, Q-  
158 Lab, Cleveland, OH) on a shelf in an environmental control room and irradiated continuously for  
159 four months (“UV exposure” treatment). The locations of three envelopes on the same shelf were  
160 rearranged every week to account for slight spatial variability in radiation intensity under the UV  
161 lamps. Three shelves were constructed to treat a total of 9 envelopes. Shelves were separated  
162 from each other with black stage curtain. A broadband radiometer with two sensors (UV-X, UV  
163 Products, Upland, CA) was used to monitor the UV radiation intensity that samples received in  
164 the UV-A and UV-B ranges. The UV-A sensor was calibrated to measure UV radiation centered



165 at 365 nm with a response curve ranging from 300 to 400 nm. The UV-B sensor was calibrated to  
166 measure UV radiation centered at 310 nm with a response curve encompassing 260 to 370 nm.  
167 Factory calibration of the UV sensors is traceable to the National Institute of Standards and  
168 Technology (NIST). The dose of UV radiation is comparable to that from past laboratory studies  
169 (Brandt et al., 2009; Lambie et al., 2014; van Asperen et al., 2015; see Results for details). The  
170 UV lamps were pre-burned for five days to stabilize radiation output. Radiation intensity was  
171 monitored periodically with the broadband radiometer, and no significant change was detected  
172 during the experiment. Note that UV lamps did emit a small amount of radiation in the visible and  
173 UV-C (< 280 nm, known to kill or inactivate microbes) ranges, which was assumed to have  
174 minor impacts on decomposition processes. The other 9 envelopes were kept in the dark inside a  
175 cardboard box in the same environmental control room (“control” treatment). Room temperature  
176 was cycled between 21 and 29 °C every 12 h. After the treatments, litter samples were dried in  
177 the oven at 60 °C, weighed to assess mass loss, and ground with a Wiley mill (Thomas Scientific,  
178 Swedesboro, NJ) through a standard US #20 mesh screen for further analyses.

179 *Litter chemistry.* For 2D NMR analyses, we included the 18 samples exposed to UV exposure  
180 and control treatments in the experiment above. To compare the effects of abiotic UV  
181 photodegradation versus microbial decomposition on litter chemistry, we also collected spectra  
182 from nine samples ( $n = 3$  from each species) that experienced microbial decomposition.  
183 Specifically, we took subsamples from the nine litter samples from the control treatment in the  
184 above experiment and incubated them with microbial inoculum for one month. Microbial  
185 inoculum was made by mixing 30 g of fresh soil from the field site with 1 L of deionized water  
186 on a bench shaker for 2 h and then filtering the mixture through a Whatman 40 filter paper to  
187 remove soil particles. One gram of litter was placed in a 50-mL plastic beaker with 3 mL of  
188 inoculum and loosely covered with laboratory film (Parafilm PM996, Bemis Company, Inc.,  
189 Neenah, WI) to minimize evaporation. The film cover was periodically removed to avoid

190 excessive accumulation of CO<sub>2</sub> in the headspace. After one month, litter was oven-dried for 2D  
191 NMR analysis.

192 All 27 of these samples were evaluated for litter chemical characteristics using 2D <sup>1</sup>H–<sup>13</sup>C  
193 heteronuclear single-quantum coherence (HSQC) spectroscopy. The 2D NMR spectra of litter  
194 cell wall material were collected following the protocol outlined in Kim and Ralph (2010) and  
195 Mansfield et al. (2012). Briefly, litter cell wall material was isolated from litter subsamples using  
196 a series of solvent extractions with water, 80% (vol/vol) ethanol, and acetone. The extraction  
197 removes soluble compounds that may distort the NMR spectra of litter cell walls. Subsamples of  
198 the extracted cell wall material (~250 mg) were finely ground using a ball-mill (Planetary Micro  
199 Mill Pulverisette 7 premium line, Fritsch, Idar-Oberstein, Germany). Then, 50 mg of ball-milled  
200 cell wall material were swelled in 500 μL of 4:1 dimethylsulfoxide (DMSO-d<sub>6</sub>)/pyridine-d<sub>5</sub>  
201 (vol/vol) to form a gel in a 5-mm NMR tube. The HSQC NMR spectroscopy was performed as  
202 described previously (Mansfield et al., 2012) on a Bruker AVANCE 700 Spectrometer (700  
203 MHz; Rheinstetten, Germany) with a cryogenically-cooled triple-resonance inverse NMR probe.  
204 Central peaks of the DMSO solvent were used as internal reference (δ<sub>H</sub> 2.50, δ<sub>C</sub> 39.5 ppm).  
205 Resonance assignments of lignin syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) units,  
206 lignin methoxyl (OMe), the α-position of the lignin β-aryl-ether (A<sub>α</sub>), and acetylated xylan units  
207 (2-*O*-Ac-β-D-Xylp and 3-*O*-Ac-β-D-Xylp) were confirmed by comparison with previously  
208 reported spectra (Ralph et al., 2009; Kim and Ralph, 2010; Talbot et al., 2011; Lan et al., 2015;  
209 Lin et al., 2015a). Lignin polymers are composed of S, G, and H monomers that are connected by  
210 several inter-unit linkages, including A<sub>α</sub>. Acetylated xylan units are key characteristics of  
211 hemicelluloses. Relative abundances of A<sub>α</sub>, 2-*O*-Ac-β-D-Xylp, and 3-*O*-Ac-β-D-Xylp were  
212 estimated by dividing their integrals by the integral of OMe, as OMe has been found to be  
213 relatively stable during the early stages of litter decomposition (Lundquist and Lundgren, 1972;  
214 Yelle et al., 2013). Relative abundances of lignin S, G, and H units were estimated by calculating

215 the ratio of each individual integral over the sum of the three integrals. However, high waxes  
216 and/or cutin levels in the *Q. douglasii* litter made it impossible to quantify lignin H units because  
217 the contours of these structures overlap with each other. Thus we only quantified lignin S and G  
218 units of *Q. douglasii*.

219 *Litter degradability.* Besides litter chemistry, we also evaluated the biodegradability of litter  
220 that had been previously exposed to the UV exposure or control treatments. A subsample (0.25 g)  
221 from each of the 18 samples was placed in a 50-mL plastic beaker. Note that this is a separate set  
222 of samples from those used for chemical analysis. Microbial inoculum (1.0 mL), which was  
223 prepared in the same fashion as described above, was added to each beaker to introduce a uniform  
224 group of microbial decomposers. The 50-mL beakers were placed into 473-mL glass jars, sealed,  
225 and incubated for 86 days in the dark in the environmental control room described above. Litter  
226 biodegradability was estimated by measuring the microbial CO<sub>2</sub> production during the  
227 incubation. Every two to four days, 1 mL of headspace was collected using a syringe and needle  
228 through a butyl rubber septum on the lid and analyzed for CO<sub>2</sub> concentration using an infrared  
229 gas analyzer (LI-COR 6252, LI-COR Corporation, Lincoln, NE). At each sampling date, a four-  
230 point calibration curve was built to standardize CO<sub>2</sub> measurements. Microcosm headspace was  
231 flushed periodically with a tank of compressed air to prevent the headspace CO<sub>2</sub> concentration  
232 from exceeding 1%. On sampling dates when the headspace was not flushed, 1 mL of CO<sub>2</sub>-free  
233 air was extracted from a column filled with soda lime and injected in each microcosm to balance  
234 pressure. Headspace CO<sub>2</sub> content (in µg) was calculated using the ideal gas law under ambient  
235 environmental conditions. Microbial CO<sub>2</sub> production was estimated using the net CO<sub>2</sub>  
236 accumulation in the headspace. Litter samples also received 1 mL of deionized water  
237 approximately every 15 days during the 86-day incubation to account for loss of water through  
238 evaporation and headspace venting.

239 2.3. Short-term photoprimering experiment

240 To assess photoprimering on a timescale of days, we established a factorial design with two  
241 levels of moisture conditions (wet and dry) and two radiation regimes: alternating between UV  
242 exposure and darkness (“alternating” treatment), and continuous darkness (“dark” treatment). We  
243 used only *B. diandrus* litter for this experiment. Litter was cut into small pieces of roughly 1 cm  
244 length and placed in 473-mL glass jars. Each microcosm received 1.0 g of litter that fully covered  
245 the jar bottom without significant overlap. Litter in the wet treatment received 2 mL of microbial  
246 inoculum that was prepared as described above, while litter in the dry treatment was kept dry.  
247 Glass jars were fitted with lids made of UV-transparent SUVT plastic (0.32 cm thickness,  
248 Spartech Polycast, Stamford, CT), which transmits at least 90% of UV radiation, and then sealed  
249 with clear silicon caulk (GE5060, General Electric Company, Huntersville, NC). The silicon  
250 caulk was allowed to cure overnight before the start of the experiment. A total of 20 microcosms  
251 were prepared ( $n = 5$ ) and half of them received an alternating cycle of UV exposure phase and  
252 dark phase. In the UV exposure phase, microcosms were placed 2 cm under a set of four UV  
253 lamps for two days in the environmental control room described above. The distance between UV  
254 lamps and litter was approximately 16 cm. The UV lamps were pre-burned for five days to  
255 stabilize radiation output. In the dark phase, microcosms were moved to a closed cardboard box  
256 in the same room for two days. Microcosms in the dark treatment were kept in another closed  
257 cardboard box continuously during the whole experiment. Our UV lamps did emit a small amount  
258 of visible light that was assumed to have limited effects on litter decomposition. We acknowledge  
259 that filtered lamps (i.e. UV radiation was filtered) would have provided a more rigid control than  
260 continuous darkness. Two empty microcosms were constructed as blanks and treated as those in  
261 the alternating treatment. Radiation intensity was monitored periodically with the broadband  
262 radiometer. Half of the lamps were replaced with pre-burned ones at around Day 40 of the  
263 experiment.

264 Every two days, we measured the headspace CO<sub>2</sub> content of all microcosms using the method  
265 described above for a total period of 128 days. As is standard practice for litter incubation studies,  
266 the CO<sub>2</sub> production rate was expressed based on the initial litter mass because there was no  
267 practical way to continuously measure the dry weights of litter samples throughout the  
268 incubation. Because of the high CO<sub>2</sub> production rate, the headspace of microcosms in the wet  
269 treatment was flushed using a tank of compressed air every two days until Day 60 of the  
270 experiment and every four days thereafter. Headspace CO<sub>2</sub> concentration accumulated very  
271 slowly in microcosms in the dry treatment, thus flushing was conducted only twice during the  
272 entire experiment (Days 78 and 94). To maintain the moisture conditions, the wet treatment  
273 received 1 ml of deionized water on five occasions (Days 44, 60, 78, 94, and 114). On Day 12 of  
274 the experiment, microcosms received two extra days of UV exposure due to an error; we decided  
275 to keep these microcosms in the dark for the next four days to keep the total duration of UV and  
276 dark phases equal.

277 To assess the impacts of UV exposure on temperature, we placed iButton temperature sensors  
278 ( $n = 3$  for both the alternating and dark treatments; DS1921, Maxim Integrated, San Jose, CA) at  
279 the bottom of empty glass microcosms and sealed them in the same way as described above.  
280 These microcosms were exposed to treatments between Day 26 to Day 40. On average, we  
281 observed that UV exposure increased air temperature by up to 2 °C. To control for the effects of  
282 temperature on decomposition, we raised the temperature of the microcosms in the dark treatment  
283 by 2 °C by placing them in a dark, controlled-temperature incubator (Lab-Line Instruments,  
284 Dubuque, IA) during the UV phase for Days 94 to 114 of the experiment. During the dark phase,  
285 microcosms were removed from the incubator and placed in a cardboard box in the environmental  
286 control room. This allowed the alternating and dark treatments to experience the same  
287 temperature fluctuations during Days 94 to 114 of the experiment. The effectiveness of the  
288 temperature control was confirmed with iButton sensors in two empty microcosms.

289 At the end of the experiment (128 days), litter pieces were carefully taken out of the  
290 microcosms using tweezers, placed in aluminum weighing dishes, and oven-dried at 60 °C for  
291 two days. Litter dry weight was recorded. A subsample (100 mg) was added to 50 mL deionized  
292 water and soaked for 24 h at 4 °C. The leachate was filtered through a glass microfiber filter  
293 (Type A/E, Pall Corporation, Port Washington, NY) and then analyzed for dissolved organic C  
294 and N concentrations via a Total Organic Carbon/Nitrogen analyzer (Series V, Shimadzu  
295 Corporation, Kyoto, Japan) with potassium biphthalate used to build standard curves.

#### 296 2.4. Statistical analyses

297 In the two-phase photoprimering experiment, effects of UV exposure on litter mass loss and  
298 biodegradability were assessed using T-tests for each of the three species. We chose the T-tests  
299 instead of multiple range tests (e.g. the Tukey's test) because we were mainly interested in the  
300 UV effects but not the relative differences among three types of litter. Effects of UV exposure  
301 and microbial decomposition on the NMR-derived cell wall characteristics were compared using  
302 one-way analysis of variance (ANOVA) per species followed by Tukey's tests. In the short-term  
303 photoprimering experiment, cumulative and instantaneous CO<sub>2</sub> production and dissolved organic C  
304 and N concentrations of litter were compared using two-way ANOVAs. T-tests were then used to  
305 examine the effects of radiation exposure since ANOVA revealed order-of-magnitude differences  
306 between dry and wet treatments. All statistical analyses were conducted in R (R Development  
307 Core Team, 2016).

### 308 **3. Results**

#### 309 3.1 Two-phase photoprimering

310 Four months of UV exposure in the laboratory increased the mass loss of the *B. diandrus* and  
311 *Q. douglasii* litter by absolute magnitudes of 3.3% and 4.0% compared to the dark control,  
312 respectively (Fig. 1a, T-tests,  $P = 0.023$  and  $0.004$ , respectively). The UV exposure treatment also

313 tended to increase the mass loss of *A. fatua*, although this effect was not statistically significant  
314 (T-test,  $P = 0.274$ ). Litter in the UV exposure treatment received average radiation levels of 11.5  
315  $\text{W m}^{-2}$  and 3.3  $\text{W m}^{-2}$  in the UV-B and UV-A ranges, respectively. During the experiment, the  
316 amount of UV radiation received by the litter samples (i.e. UV exposure received by both sides of  
317 litter envelopes) corresponded to four months of UV radiation (from July to October) measured at  
318 Sedgwick Reserve. The UV exposure treatment, however, did not affect litter biodegradability:  
319 none of the three types of litter showed differences in cumulative  $\text{CO}_2$  production between the  
320 UV exposure and control treatments during an incubation with microbial inoculum (Fig. 1b). The  
321 peak of instantaneous  $\text{CO}_2$  production was temporally delayed under UV exposure compared to  
322 the control in all three species (Fig. S1). Once the instantaneous  $\text{CO}_2$  production rates stabilized,  
323 there was no difference between the UV exposure and control treatments.

324 After four months of UV exposure, the *B. diandrus* litter still exhibited 2D NMR spectra that  
325 were similar to those observed in the control samples (Fig. 2). In contrast, one month of microbial  
326 degradation drastically altered the 2D NMR spectra of litter cell walls: microbial degradation  
327 strongly reduced the relative signal intensity of the lignin  $\beta$ -aryl ethers ( $A_\alpha$  and  $A_{\beta-S}$ ), which are  
328 the dominant type of lignin inter-unit linkages, and reduced acetylated xylans (*2-O-Ac- $\beta$ -D-Xylp*  
329 and *3-O-Ac- $\beta$ -D-Xylp*) compared to the reference samples in the aliphatic region. Aromatic  
330 signals corresponding to lignin H units and triclin almost disappeared in the microbially degraded  
331 samples, and microbial degradation consistently broadened NMR contours, a phenomenon  
332 commonly observed in samples that have experienced significant chemical or biological  
333 degradation (Samuel et al., 2011; Yelle et al., 2013; Lin et al., 2015a).

334 Quantification of the NMR spectra further confirmed that one month of microbial  
335 decomposition strongly reduced the relative abundances of lignin  $\beta$ -aryl ethers ( $A_\alpha$ ), acetylated  
336 xylans (*2-O-Ac- $\beta$ -D-Xylp* and *3-O-Ac- $\beta$ -D-Xylp*), and lignin H units in *B. diandrus* relative to the  
337 control (Fig. 3, Tukey's tests, all  $P < 0.05$ ). The UV exposure, on the contrary, did not influence

338 abundances of  $A_{\alpha}$  and 3-*O*-Ac- $\beta$ -<sub>D</sub>-Xylp in *B. diandrus* and even increased the apparent levels of  
339 2-*O*-Ac- $\beta$ -<sub>D</sub>-Xylp and H units in *B. diandrus* relative to the control (Tukey's tests,  $P = 0.024$  and  
340 0.031, respectively). In *A. fatua*, microbial incubation also decreased the level of 2-*O*-Ac- $\beta$ -<sub>D</sub>-  
341 Xylp compared to the control (Tukey's test,  $P < 0.001$ ), whereas UV exposure increased it  
342 (Tukey's test,  $P = 0.039$ ). Both UV exposure and microbial treatments also increased lignin H  
343 units in *A. fatua* relative to the control (Tukey's tests,  $P = 0.019$  and 0.024, respectively).  
344 Compared to *B. diandrus* and *A. fatua*, litter chemistry of *Q. douglasii* was less responsive to the  
345 UV exposure and microbial treatments. The only statistically significant effect on *Q. douglasii*  
346 was that UV exposure increased 3-*O*-Ac- $\beta$ -<sub>D</sub>-Xylp relative to control and microbial treatments  
347 (Tukey's tests,  $P = 0.005$  and 0.006, respectively).

### 348 3.2. Short-term photoprimering

349 Mass loss and 128-day cumulative CO<sub>2</sub> production showed similar responses to light regime  
350 and moisture treatments. Mass loss was much lower in the dry treatment than in the wet treatment  
351 (mean±S.E: 6.8±1.0% versus 43.7±0.6%), but it was not affected by light regime under either dry  
352 or wet conditions (data not shown). Cumulative CO<sub>2</sub> production was at least two orders of  
353 magnitude lower in the dry treatment than in the wet treatment (Fig. 4a). After accounting for the  
354 CO<sub>2</sub> emission from the blanks, which received the same pattern of UV exposure as the alternating  
355 treatment, there was no observable difference in CO<sub>2</sub> production from the dry litter between the  
356 alternating and the dark treatments. In the wet treatment, there was also no difference in  
357 cumulative CO<sub>2</sub> production between the alternating and dark treatments. However, from Day 65  
358 to 128, the alternating treatment increased the cumulative CO<sub>2</sub> production from wet litter by 35%  
359 relative to the dark treatment (Fig. 4b, T-test,  $P < 0.001$ ). In the same period, the increases in  
360 cumulative CO<sub>2</sub> production induced by the alternating treatment were statistically significant  
361 both during the UV exposure phase (15.4 vs. 10.6 mg C g<sup>-1</sup> litter; T-test,  $P < 0.001$ ) and during  
362 the dark phase (15.7 vs. 12.2 mg C g<sup>-1</sup> litter; T-test,  $P = 0.005$ ). Litter in the UV exposure



363 treatment received approximately  $4.1 \text{ W m}^{-2}$  and  $1.1 \text{ W m}^{-2}$  in the UV-B and UV-A ranges,  
364 respectively.

365 When the litter was wet, temporal patterns of instantaneous  $\text{CO}_2$  production further illustrated  
366 how the alternating treatment influenced litter decomposition (Fig. 5). On the first sampling day,  
367 the litter  $\text{CO}_2$  production rate was higher in the dark than in the alternating treatment (T-test,  $P =$   
368  $0.021$ ). On the next two sampling days, the  $\text{CO}_2$  production rate decreased in the dark treatment,  
369 while it increased in the alternating treatment. Between Days 4 and 76, there was no statistical  
370 difference in  $\text{CO}_2$  production rate between the two light regime treatments, although on multiple  
371 occasions (e.g. Days 18, 34, 66, and 68), the alternating treatment tended to have higher  $\text{CO}_2$   
372 production in the UV phase. After the second event of water addition and between Days 78 and  
373 94, the alternating treatment showed elevated litter  $\text{CO}_2$  production in the UV phase relative to  
374 the dark treatment (T-tests,  $P < 0.05$ ). After Day 98, the alternating treatment showed a  
375 consistently higher  $\text{CO}_2$  production rate in both the UV and dark phases compared to the dark  
376 treatment (T-tests,  $P < 0.05$ ). At the end of the experiment, we found that litter in the alternating  
377 treatment had higher dissolved organic C (DOC) concentration than that in the dark treatment  
378 when litter was wet (Fig. 4c, T-test,  $P = 0.072$ ), though there was no difference in DOC  
379 concentration between the alternating and dark treatments when litter was dry. Dissolved organic  
380 N (DON) concentration of litter was not different between experimental treatments at the end of  
381 the incubation (data not shown).

## 382 **4. Discussion**

### 383 4.1. Two-phase photoprimering

384 Four months of continuous UV exposure induced significant litter mass loss in two out of  
385 three species of dry litter (Fig. 1a), suggesting that abiotic photodegradation contributed to litter  
386 decomposition. The UV-induced increase in mass loss was around 3-4% over the four-month

387 period. This result suggests that the non-biological contribution of UV photodegradation to mass  
388 loss is small in magnitude, which is consistent with a meta-analysis that assessed the effect of  
389 abiotic photodegradation on litter mass loss (Wang et al., 2015). We also observed a small but  
390 significant amount of litter mass loss in the dark treatment (4-6%). Although litter was oven-dried  
391 prior to the experiment, it might have absorbed moisture from the air during the experiment,  
392 which could enable microbial decomposition (Dirks et al., 2010).

393 Previous studies have reported that UV radiation facilitated subsequent microbial litter  
394 decomposition (Foereid et al., 2010; Gaxiola and Armesto, 2015; Wang et al., 2015; Yanni et al.,  
395 2015). We did not find significant photopriming effects on the degradability of any of the three  
396 litter types after four months of UV exposure (Fig. 1b). This result is consistent with our previous  
397 results (Lin et al., 2015b), showing that up to one year of field UV exposure did not increase the  
398 biodegradability of *B. diandrus*. Other studies have also reported negligible effects of UV  
399 exposure on subsequent microbial decomposition of litter in the laboratory (Brandt et al., 2009;  
400 Lambie et al., 2014). We found that UV exposure treatment consistently delayed the peak of  
401 instantaneous microbial respiration from all litter types (Fig. S1), suggesting that continuous UV  
402 exposure inhibited the colonization and growth of microbes from the inoculum onto the litter  
403 material. This negative effect could offset the potential positive effect of UV exposure on litter  
404 degradability, resulting in a lack of photopriming. The photopriming effect may also depend on  
405 the spectral region of radiation. Austin et al. (2016) found that exposure to UV radiation inhibited  
406 subsequent microbial decomposition for a group of woody species, while exposure to visible  
407 (blue-green) light increased the microbial degradability of these species. Consistent with these  
408 studies, our results indicate that four months of exposure to UV radiation does not necessarily  
409 increase litter biodegradability. Our NMR analyses revealed that four months of UV exposure had  
410 very limited effects on lignin and hemicellulose in litter cell walls (Figs. 2 and 3), again  
411 demonstrating that abiotic UV photodegradation is not necessarily sufficient for altering litter

412 chemistry or biodegradability. These results also led us to examine whether photopriming might  
413 occur on a shorter timescale (e.g. daily or diel).

#### 414 4.2. Short-term photopriming

415 Our results show that litter CO<sub>2</sub> production was enhanced by the alternating treatment relative  
416 to the dark control when litter was wet (Figs. 4 and 5). We attribute these increases in CO<sub>2</sub>  
417 production rates to microbial decomposition, as abiotic UV photodegradation was not effective in  
418 inducing significant CO<sub>2</sub> production during this experiment (Fig. 4a). The UV-induced increase  
419 in litter decomposition could not be explained by minor temperature differences between the  
420 treatments, as the effect persisted even after raising the temperature of the dark treatment between  
421 Days 94 to 114. Instead our results indicate strong interactions between abiotic and biotic  
422 decomposition mechanisms when they operate in concert on daily, as opposed to monthly,  
423 timescales. We observed photopriming effects of UV exposure on microbial decomposition, as  
424 the alternating treatment increased litter decomposition relative to the dark treatment even during  
425 periods when litter did not receive UV radiation (Fig. 5, after Day 96). It is likely that prior UV  
426 exposure in the alternating treatment increased the level of labile substrates available for  
427 microbial decomposition. Our DOC results indeed support this mechanism, as the alternating  
428 treatment showed higher extractable DOC than the dark treatment when litter was wet (Fig. 4c).  
429 Exposure of litter to UV radiation could increase the potential activities of microbial extracellular  
430 enzymes in degrading litter substrates such as hemicellulose and lignin (Baker and Allison, 2015)  
431 and consequently promote litter decomposition and the accumulation of labile C. Effects of UV  
432 exposure on litter chemistry, despite being small in magnitude (Fig. 3), might also provide a  
433 positive feedback to microbial decomposition by making litter substrates more accessible to  
434 microbial decomposers.

435 As in the two-phase experiment, we found evidence of UV inhibition effects on microbial  
436 respiration, as the peak of CO<sub>2</sub> production rate was delayed in the alternating treatment relative to

437 the dark treatment at the beginning of the experiment (Fig. 5). Similar negative effects of UV  
438 exposure have been reported by several photodegradation studies (Smith et al., 2010; Lambie et  
439 al., 2014; Lin et al., 2015b). Because our UV lamps were used without diacetate film, litter  
440 samples could be exposed to a small amount of UV-C radiation that further amplified these  
441 negative effects on microbes. Continuous UV exposure likely enhanced the inhibition effects,  
442 resulting in more significant delays of microbial respiration in the two-phase experiment than in  
443 the short-term experiment (Figs. 5 and S1). Alternating UV exposure with dark conditions, on the  
444 other hand, could provide reoccurring time windows to allow microbial decomposers to recover  
445 from the UV inhibition effects. The alternating light regime could thus be the key to minimizing  
446 the UV inhibition effects and enabling a synergy between abiotic photodegradation and microbial  
447 decomposition. The role of light regime (e.g. continuous versus alternating; different frequencies)  
448 in mediating the various effects of UV radiation deserves further attention, as recent modeling  
449 work suggests that the UV inhibition effect likely occurs simultaneously with photopriming  
450 during litter photodegradation (Adair et al., 2017).

451 The above results illustrate a pathway through which UV photodegradation increases litter  
452 microbial decomposition on a temporal scale of days. Gliksman et al. (2016) reported similar  
453 short-term dynamics between abiotic and biotic decay processes during the dry season in a  
454 Mediterranean shrubland. They found significant mutual enhancement between photodegradation  
455 in the day and microbial decomposition at night, suggesting that both photopriming and microbial  
456 priming of photodegradation occurred at a diel scale. In their study, litter decomposition was  
457 strongly regulated by diel variations in humidity, as litter humidity fluctuated between a low level  
458 in the day and a high level at night Gliksman et al. (2016). Litter moisture in our experiment was  
459 maintained at a relatively high level by regular addition of water. We found that the magnitude of  
460 the UV effects on litter decomposition tended to be amplified by water addition. Water addition  
461 likely increased the accessibility of litter substrates to microbial decomposers by mobilizing both

462 microbes and their substrates, and water addition consequently enhanced the positive interaction  
463 between photodegradation and microbial decomposition. Thus our results imply that positive  
464 interactions between UV photodegradation and microbial decomposition are not limited to arid  
465 areas. As discussed earlier, the alternating light regime, rather than the prevailing moisture  
466 conditions, is perhaps more important in stimulating photoprimering effects.

467 Although the UV lamps used in our experiments did not emit significant visible radiation  
468 (Majer and Hideg, 2012), we speculate that short-term photoprimering could be triggered by visible  
469 light. Recent studies have increasingly recognized the importance of visible light in inducing  
470 photodegradation (Day et al., 2015; Austin et al., 2016). Future studies should explore the relative  
471 effectiveness of visible versus UV radiation during short-term photoprimering. We also recognize  
472 that the alternating treatment did not affect the cumulative CO<sub>2</sub> production of wet litter over the  
473 entire experiment (Fig. 4a), as there was no response of microbial respiration to the alternating  
474 treatment in the first 74 days of the experiment (Fig. 5). Decomposition of labile substrates,  
475 which dominates during the early stages of decomposition, is likely to be controlled by biotic  
476 decomposition mechanisms and to be less responsive to photodegradation relative to the  
477 decomposition of structural carbohydrates and lignin. It is possible that the facilitation effect of  
478 UV radiation on microbial respiration is relatively small in magnitude compared to the gross rate  
479 of microbial decomposition early in the experiment (e.g., the first 40 days). It is also possible that  
480 the inhibitory effects of UV radiation on microbial activity counteracted the photoprimering effects  
481 early on during the experiment. Thus photoprimering only became significant when the rate of  
482 microbial respiration dropped below a critical threshold or when the microbial community  
483 became adapted to UV radiation.

#### 484 4.3. Lignin degradation

485 In contrast to our initial hypothesis, microbial decomposition was much more effective than  
486 abiotic photodegradation in degrading litter cell walls, particularly targeting lignin  $\beta$ -aryl ethers,

487 H units, and acetylated xylans in *B. diandrus* (Figs. 2 and 3). Despite the large amount of UV  
488 radiation received by litter samples, which corresponded to four months of UV exposure at peak  
489 intensity at our field site (July to October), no lignin or hemicellulose feature was degraded by  
490 UV exposure in all studied litter species (Fig. 3). These results indicate that continuous UV  
491 exposure is not particularly effective in degrading lignin or hemicelluloses, which is also  
492 consistent with the negligible or small effects of UV exposure on litter mass loss and CO<sub>2</sub>  
493 production (Figs. 1a and 4a). Our findings thus challenge the conventional view that abiotic  
494 processes are the primary factor in breaking down lignin and subsequently facilitating microbial  
495 decomposition.

496 Surprisingly, the pattern of changes in NMR spectra induced by microbial decomposition  
497 matched nicely with those induced by UV exposure in the field, as reported by our previous study  
498 (Lin et al., 2015a). In particular lignin β-aryl ethers, H units, and acetylated xylans in *B. diandrus*  
499 were degraded by both one year of UV exposure in the field (Lin et al., 2015a) and microbial  
500 decomposition in the laboratory (Figs. 2 and 3). This surprising result suggests that microbial  
501 decomposition was ultimately responsible for the UV effects observed in the field. Short-term  
502 facilitation could reasonably explain this dominant role of microbial decomposition in degrading  
503 lignin. Under field conditions, UV exposure in the day could enhance litter microbial  
504 decomposition at night, thus creating short-term facilitation effects on a diel scale.

505 Together with our past research (Lin et al., 2015a), the new results from the NMR analyses  
506 (Figs. 2 and 3) and short-term photoprimering experiments (Figs. 4 and 5) indicate that abiotic  
507 photodegradation alone does not explain the UV-induced changes in lignin and hemicellulose  
508 observed in the field; instead, these changes were likely caused by microbial decomposition that  
509 was ‘photoprimered’ by UV radiation. Our results therefore have important implications for  
510 interpreting results from previously published studies on litter photodegradation. Most of the  
511 previous field studies did not explicitly suppress biotic decomposition (reviewed by King et al.,

512 2012; Song et al., 2013), thus they could not differentiate the contribution of abiotic  
513 photodegradation vs. photopriming to litter decomposition. Therefore, the effects of radiation  
514 manipulation on litter decomposition processes observed in these studies should be interpreted as  
515 the combined effects of abiotic photodegradation and photopriming, rather than a pure abiotic  
516 effect. Together with several recent studies (Wang et al., 2015; Austin et al., 2016; Glikzman et  
517 al., 2016), our work further suggests that photopriming should account for a large proportion, if  
518 not the majority, of the reported litter mass loss and changes in litter chemistry induced by  
519 photodegradation. In order to improve the predictions of decomposition rates and C fluxes,  
520 biogeochemical models should preferentially incorporate photopriming mechanisms, particularly  
521 on diel or at daily timescales, rather than abiotic processes (e.g., Adair et al., 2017).

522 Our NMR analyses also reveal that microbial decomposition has species-specific effects on  
523 litter chemistry. For instance, microbial decomposition degraded acetylated xylans of two grass  
524 litters, *B. diandrus* and *A. fatua*, but did not affect those of a tree leaf, *Q. douglasii* (Fig. 3). As  
525 the incubation period lasted only 86 days, these litter samples were probably still in the early  
526 stage of decomposition in which labile substrates were primarily being degraded. Differences in  
527 the composition of labile substrates and cell wall components among the three species are likely  
528 responsible for the observed variations in their responses to microbial decomposition. In addition  
529 to these species-specific effects, we also found that UV exposure sometimes slightly increased the  
530 relative abundances of certain chemical structures (e.g. 2-O-Ac- $\beta$ -D-Xylp in *A. fatua* and *B.*  
531 *diandrus*; Fig. 3b). The exact mechanisms behind these effects are unclear. When quantifying  
532 acetylated xylan, we calculated its ratio over the lignin methoxyl (OMe) and assumed that lignin  
533 methoxyl remained stable during UV photodegradation and microbial decomposition. It is  
534 possible that our assumption was not entirely valid for UV photodegradation, as photochemical  
535 reactions might preferentially target OMe relative to the acetylated xylan.

536 5. Conclusions

537 Our study showed that four months of exposure to UV radiation led to litter mass loss that was  
538 statistically greater than the control, though the changes were small in magnitude. Results of our  
539 short-term photoprimering experiment further illustrate that the photoprimering effect can occur on a  
540 timescale of days. An alternating light regime at the timescale of days may be critical for  
541 reducing UV inhibition effects on microbes and for creating the synergy between UV radiation  
542 and microbial decomposition. Microbial decomposition, rather than abiotic UV photodegradation,  
543 explained the UV-induced changes in litter chemistry previously observed in a field experiment.  
544 To our knowledge, our results are the first to provide chemical evidence that photoprimering is  
545 primarily responsible for breaking down lignin and hemicellulose during photodegradation. We  
546 propose short-term photoprimering as a key mechanism during litter decomposition in a wide range  
547 of environmental conditions. The results of our work have strong implications for how  
548 photodegradation and microbial processes should be represented in models to accurately predict  
549 decomposition and ecosystem C cycling.

550

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563 **References**

- 564 Adair, E.C., Parton, W.J., Del Grosso, S.J., Silver, W.L., Harmon, M.E., Hall, S.A., Burke, I.C.,  
 565 Hart, S.C., 2008. Simple three - pool model accurately describes patterns of long - term  
 566 litter decomposition in diverse climates. *Global Change Biology* 14, 2636-2660.
- 567 Adair, E.C., Parton, W.J., King, J.Y., Brandt, L.A., Lin, Y., 2017. Accounting for  
 568 photodegradation dramatically improves prediction of carbon losses in dryland systems.  
 569 *Ecosphere* 8, e01892-e01892.
- 570 Austin, A.T., Ballaré, C.L., 2010. Dual role of lignin in plant litter decomposition in terrestrial  
 571 ecosystems. *Proceedings of the National Academy of Sciences, USA* 107, 2-6.
- 572 Austin, A.T., Méndez, M.S., Ballaré, C.L., 2016. Photodegradation alleviates the lignin  
 573 bottleneck for carbon turnover in terrestrial ecosystems. *Proceedings of the National*  
 574 *Academy of Sciences*, 4392-4397.
- 575 Austin, A.T., Vivanco, L., 2006. Plant litter decomposition in a semi-arid ecosystem controlled  
 576 by photodegradation. *Nature* 442, 555-558.
- 577 Baker, N.R., Allison, S.D., 2015. Ultraviolet photodegradation facilitates microbial litter  
 578 decomposition in a Mediterranean climate. *Ecology* 96, 1994-2003.
- 579 Barnes, P.W., Throop, H.L., Archer, S.R., Breshears, D.D., McCulley, R.L., Tobler, M.A., 2015.  
 580 Sunlight and soil-litter mixing: drivers of litter decomposition in drylands, *Progress in*  
 581 *Botany*. Springer, pp. 273-302.
- 582 Berg, B., McLaugherty, C., 2008. *Plant litter: decomposition, humus formation, carbon*  
 583 *sequestration*. Springer-Verlag, Berlin, Heidelberg, Germany.
- 584 Brandt, L.A., Bohnet, C., King, J.Y., 2009. Photochemically induced carbon dioxide production  
 585 as a mechanism for carbon loss from plant litter in arid ecosystems. *Journal of*  
 586 *Geophysical Research-Biogeosciences* 114, G02004.
- 587 Brandt, L.A., King, J.Y., Hobbie, S.E., Milchunas, D.G., Sinsabaugh, R.L., 2010. The role of  
 588 photodegradation in surface litter decomposition across a grassland ecosystem  
 589 precipitation gradient. *Ecosystems* 13, 765-781.
- 590 Brandt, L.A., King, J.Y., Milchunas, D.G., 2007. Effects of ultraviolet radiation on litter  
 591 decomposition depend on precipitation and litter chemistry in a shortgrass steppe  
 592 ecosystem. *Global Change Biology* 13, 2193-2205.
- 593 Carvalhais, N., Forkel, M., Khomik, M., Bellarby, J., Jung, M., Migliavacca, M., Mu, M.,  
 594 Saatchi, S., Santoro, M., Thurner, M., 2014. Global covariation of carbon turnover times  
 595 with climate in terrestrial ecosystems. *Nature* 514, 213-217.
- 596 Coûteaux, M.-M., Bottner, P., Berg, B., 1995. Litter decomposition, climate and litter quality.  
 597 *Trends in Ecology & Evolution* 10, 63-66.
- 598 Day, T.A., Guénon, R., Ruhland, C.T., 2015. Photodegradation of plant litter in the Sonoran  
 599 Desert varies by litter type and age. *Soil Biology and Biochemistry* 89, 109-122.
- 600 Day, T.A., Zhang, E.T., Ruhland, C.T., 2007. Exposure to solar UV-B radiation accelerates mass  
 601 and lignin loss of *Larrea tridentata* litter in the Sonoran Desert. *Plant Ecology* 193, 185-  
 602 194.
- 603 Dirks, I., Navon, Y., Kanas, D., Dumbur, R., Grünzweig, J., 2010. Atmospheric water vapor as  
 604 driver of litter decomposition in Mediterranean shrubland and grassland during rainless  
 605 seasons. *Global Change Biology* 16, 2799-2812.
- 606 Feng, X., Hills, K.M., Simpson, A.J., Whalen, J.K., Simpson, M.J., 2011. The role of  
 607 biodegradation and photo-oxidation in the transformation of terrigenous organic matter.  
 608 *Organic Geochemistry* 42, 262-274.
- 609 Foereid, B., Bellarby, J., Meier-Augenstein, W., Kemp, H., 2010. Does light exposure make plant  
 610 litter more degradable? *Plant and Soil* 333, 275-285.

611 Frouz, J., Cajthaml, T., Mudrak, O., 2011. The effect of lignin photodegradation on  
612 decomposability of *Calamagrostis epigeios* grass litter. *Biodegradation* 22, 1247-1254.

613 Gallo, M.E., Porras-Alfaro, A., Odenbach, K.J., Sinsabaugh, R.L., 2009. Photoacceleration of  
614 plant litter decomposition in an arid environment. *Soil Biology and Biochemistry* 41,  
615 1433-1441.

616 Gaxiola, A., Armesto, J.J., 2015. Understanding litter decomposition in semiarid ecosystems:  
617 linking leaf traits, UV exposure and rainfall variability. *Frontiers in Plant Science* 6, 1-9.

618 Gliksman, D., Rey, A., Seligmann, R., Dumbur, R., Sperling, O., Navon, Y., Haenel, S., De  
619 Angelis, P., Arnone, J.A., Grunzweig, J.M., 2016. Biotic degradation at night, abiotic  
620 degradation at day: positive feedbacks on litter decomposition in drylands. *Global*  
621 *Change Biology*, doi: 10.1111/gcb.13465.

622 Henry, H.A.L., Brizgys, K., Field, C.B., 2008. Litter decomposition in a California annual  
623 grassland: interactions between photodegradation and litter layer thickness. *Ecosystems*  
624 11, 545-554.

625 Huang, G., Zhao, H.M., Li, Y., 2017. Litter decomposition in hyper-arid deserts:  
626 Photodegradation is still important. *Science of the Total Environment* 601-602, 784-792.

627 Kim, H., Ralph, J., 2010. Solution-state 2D NMR of ball-milled plant cell wall gels in DMSO-  
628 d<sub>6</sub>/pyridine-d<sub>5</sub>. *Organic & Biomolecular Chemistry* 8, 576-591.

629 King, J.Y., Brandt, L.A., Adair, E.C., 2012. Shedding light on plant litter decomposition:  
630 advances, implications and new directions in understanding the role of photodegradation.  
631 *Biogeochemistry* 111, 57-81.

632 Kirschbaum, M.U.F., Lambie, S.M., Zhou, H., 2011. No UV enhancement of litter decomposition  
633 observed on dry samples under controlled laboratory conditions. *Soil Biology and*  
634 *Biochemistry* 43, 1300-1307.

635 Lambie, S.M.M., Kirschbaum, M.U.F.U.F., Dando, J., 2014. No photodegradation of litter and  
636 humus exposed to UV-B radiation under laboratory conditions: No effect of leaf  
637 senescence or drying temperature. *Soil Biology and Biochemistry* 69, 46-53.

638 Lan, W., Lu, F., Regner, M., Zhu, Y., Rencoret, J., Ralph, S.A., Zakai, U.I., Morreel, K., Boerjan,  
639 W., Ralph, J., 2015. Tricin, a flavonoid monomer in monocot lignification. *Plant*  
640 *Physiology* 167, 1284-1295.

641 Lee, H., Rahn, T., Throop, H., 2012. An accounting of C-based trace gas release during abiotic  
642 plant litter degradation. *Global Change Biology* 18, 1185-1195.

643 Leff, J.W., Fierer, N., 2008. Volatile organic compound (VOC) emissions from soil and litter  
644 samples. *Soil Biology and Biochemistry* 40, 1629-1636.

645 Lin, Y., King, J., 2014. Effects of UV exposure and litter position on decomposition in a  
646 California grassland. *Ecosystems* 17, 158-168.

647 Lin, Y., King, J.Y., Karlen, S.D., Ralph, J., 2015a. Using 2D NMR spectroscopy to assess effects  
648 of UV radiation on cell wall chemistry during litter decomposition. *Biogeochemistry* 125,  
649 427-436.

650 Lin, Y., Scarlett, R.D., King, J.Y., 2015b. Effects of UV photodegradation on subsequent  
651 microbial decomposition of *Bromus diandrus* litter. *Plant and Soil* 395, 263-271.

652 Liu, S., Hu, R., Cai, G., Lin, S., Zhao, J., Li, Y., 2014. The role of UV-B radiation and  
653 precipitation on straw decomposition and topsoil C turnover. *Soil Biology and*  
654 *Biochemistry* 77, 197-202.

655 Lombardozi, D.L., Bonan, G.B., Smith, N.G., Dukes, J.S., Fisher, R.A., 2015. Temperature  
656 acclimation of photosynthesis and respiration: A key uncertainty in the carbon cycle -  
657 climate feedback. *Geophysical Research Letters* 42, 8624-8631.

658 Lundquist, K., Lundgren, R., 1972. Acid degradation of lignin. *Acta Chemica Scandinavica* 26,  
659 2005-2023.

660 Majer, P., Hideg, É., 2012. Developmental stage is an important factor that determines the  
661 antioxidant responses of young and old grapevine leaves under UV irradiation in a green-  
662 house. *Plant Physiology and Biochemistry* 50, 15-23.

663 Mansfield, S.D., Kim, H., Lu, F., Ralph, J., 2012. Whole plant cell wall characterization using  
664 solution-state 2D NMR. *Nature Protocols* 7, 1579-1589.

665 Melillo, J.M., Aber, J.D., Muratore, J.F., 1982. Nitrogen and lignin control of hardwood leaf litter  
666 decomposition dynamics. *Ecology* 63, 621-626.

667 Parton, W., Silver, W.L., Burke, I.C., Grassens, L., Harmon, M.E., Currie, W.S., King, J.Y.,  
668 Adair, E.C., Brandt, L.A., Hart, S.C., 2007. Global-scale similarities in nitrogen release  
669 patterns during long-term decomposition. *Science* 315, 361-364.

670 Preston, C.M., Trofymow, J.A., 2015. The chemistry of some foliar litters and their sequential  
671 proximate analysis fractions. *Biogeochemistry* 126, 197-209.

672 R Development Core Team, 2016. R-A language and environment for statistical computing,  
673 version 3.3.1. R Foundation for Statistical Computing, Vienna, Austria.

674 Ralph, S.A., Ralph, J., Landucci, L.L., 2009. NMR database of lignin and cell wall model  
675 compounds.

676 Samuel, R., Foston, M., Jiang, N., Allison, L., Ragauskas, A.J., 2011. Structural changes in  
677 switchgrass lignin and hemicelluloses during pretreatments by NMR analysis. *Polymer*  
678 *Degradation and Stability* 96, 2002-2009.

679 Schade, G.W., Hofmann, R.-M., Crutzen, P.J., 1999. CO emissions from degrading plant matter.  
680 *Tellus. Series B: Chemical and Physical Meteorology* 51, 889-908.

681 Schaefer, D., Steinberger, Y., Whitford, W.G., 1985. The failure of nitrogen and lignin control of  
682 decomposition in a North American desert. *Oecologia* 65, 382-386.

683 Sluiter, J.B., Ruiz, R.O., Scarlata, C.J., Sluiter, A.D., Templeton, D.W., 2010. Compositional  
684 analysis of lignocellulosic feedstocks. 1. Review and description of methods. *Journal of*  
685 *Agricultural and Food Chemistry* 58, 9043-9053.

686 Smith, M.J., Purves, D.W., Vanderwel, M.C., Lyutsarev, V., Emmott, S., 2013. The climate  
687 dependence of the terrestrial carbon cycle, including parameter and structural  
688 uncertainties. *Biogeosciences* 10, 583-606.

689 Smith, W.K., Gao, W., Steltzer, H., Wallenstein, M.D., Tree, R., Resource, N., State, C., Collins,  
690 F., 2010. Moisture availability influences the effect of ultraviolet-B radiation on leaf litter  
691 decomposition. *Global Change Biology* 16, 484-495.

692 Smith, W.K., Reed, S.C., Cleveland, C.C., Ballantyne, A.P., Anderegg, W.R.L., Wieder, W.R.,  
693 Liu, Y.Y., Running, S.W., 2016. Large divergence of satellite and Earth system model  
694 estimates of global terrestrial CO<sub>2</sub> fertilization. *Nature Climate Change* 6, 306-310.

695 Song, X., Peng, C., Jiang, H., Zhu, Q., Wang, W., 2013. Direct and indirect effects of UV-B  
696 exposure on litter decomposition: a meta-analysis. *PloS One* 8, e68858.

697 Talbot, J.M., Yelle, D.J., Nowick, J., Treseder, K.K., 2011. Litter decay rates are determined by  
698 lignin chemistry. *Biogeochemistry* 108, 279-295.

699 Uselman, S.M., Snyder, K.A., Blank, R.R., Jones, T.J., 2011. UVB exposure does not accelerate  
700 rates of litter decomposition in a semi-arid riparian ecosystem. *Soil Biology and*  
701 *Biochemistry* 43, 1254-1265.

702 van Asperen, H., Warneke, T., Sabbatini, S., Nicolini, G., Papale, D., Notholt, J., 2015. The role  
703 of photo-and thermal degradation for CO<sub>2</sub> and CO fluxes in an arid ecosystem.  
704 *Biogeosciences* 12, 4161-4174.

705 Wang, J., Liu, L., Wang, X., Chen, Y., 2015. The interaction between abiotic photodegradation  
706 and microbial decomposition under ultraviolet radiation. *Global Change Biology* 21,  
707 2095-2104.

708 Whelan, M.E., Rhew, R.C., 2014. Carbonyl sulfide produced by abiotic thermal and  
709 photodegradation of soil organic matter from wheat field substrate. *Journal of*  
710 *Geophysical Research: Biogeosciences* 120, 54-62.

711 Wieder, W.R., Cleveland, C.C., Smith, W.K., Todd-Brown, K., 2015. Future productivity and  
712 carbon storage limited by terrestrial nutrient availability. *Nature Geoscience* 8, 441-444.  
713 Yanni, S.F., Suddick, E.C., Six, J., 2015. Photodegradation effects on CO<sub>2</sub> emissions from litter  
714 and SOM and photo-facilitation of microbial decomposition in a California grassland.  
715 *Soil Biology and Biochemistry* 91, 40-49.  
716 Yelle, D.J., Kaparaju, P., Hunt, C.G., Hirth, K., Kim, H., Ralph, J., Felby, C., 2013. Two-  
717 Dimensional NMR evidence for cleavage of lignin and xylan substituents in wheat straw  
718 through hydrothermal pretreatment and enzymatic hydrolysis. *BioEnergy Research* 6,  
719 211-221.

720

721

722 Figure Captions

723

724 Fig. 1. Effects of four months of UV exposure on **(a)** litter mass loss and **(b)** litter  
725 biodegradability, which was estimated by cumulative CO<sub>2</sub> production from litter during 86 days  
726 of incubation with microbial inoculum from the two-phase photopriming experiment. Error bars  
727 indicate standard errors of means ( $n = 3$ ). Different letters indicate statistical differences between  
728 the control and UV exposure treatment at  $\alpha = 0.05$  level (T-tests).

729

730 Fig. 2. Representative 2D <sup>1</sup>H–<sup>13</sup>C HSQC NMR spectra of whole-cell-wall gels of *B. diandrus*  
731 litter in DMSO-*d*<sub>6</sub>/pyridine-*d*<sub>5</sub> (4:1, vol:vol) in the aliphatic region **(a-c)** and the aromatic region  
732 **(d-f)**. Spectra are aligned to present samples from the following treatments (from L to R): control  
733 (a, d), four months of UV degradation (b, e), and one month of microbial degradation (c, f).

734

735 Fig. 3. Effects of UV and microbial degradation on the **(a)** lignin β-aryl ether (A<sub>α</sub>), **(b)** acetylated  
736 xylan (2-*O*-Ac-β-D-Xylp), **(c)** acetylated xylan (3-*O*-Ac-β-D-Xylp), and **(d)** lignin *p*-  
737 hydroxyphenyl (H) units of *A. fatua*, *B. diandrus*, and *Q. douglasii* litter. Abundances of A<sub>α</sub>, 2-*O*-  
738 Ac-β-D-Xylp, and 3-*O*-Ac-β-D-Xylp were calculated by dividing their NMR integrals relative to  
739 the integral of lignin methoxyl (OMe). Relative abundance of lignin H units was calculated by  
740 dividing its integrals by the sum of integrals of all lignin monomers. NA, levels of lignin H units  
741 could not be resolved in the spectra of the *Q. douglasii* litter. Error bars indicate standard errors  
742 of means ( $n = 3$ ). Different letters indicate statistical differences among treatments at  $\alpha = 0.05$   
743 level (Tukey's tests).

744

745 Fig. 4. Effects of dark and alternating treatments **(a)** on the cumulative CO<sub>2</sub> production in the dry  
746 and wet treatments during the 128-day short-term photopriming experiment (log scale), **(b)** on the

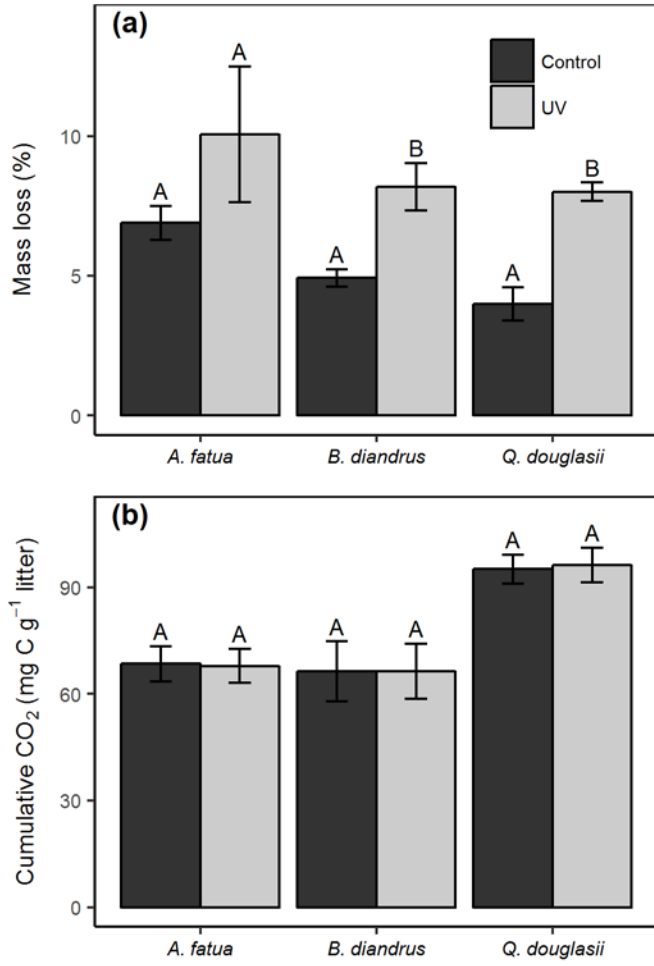
747 cumulative CO<sub>2</sub> production in the wet treatment during Days 1-64 and Days 65-128 of the  
748 experiment, and (c) on the litter dissolved organic C concentration in the dry and wet treatments  
749 at the end of the experiment. Error bars indicate standard errors of means ( $n = 5$ ). Different letters  
750 indicate statistical differences between dark and alternating treatments at  $\alpha = 0.05$  (upper case)  
751 and 0.10 (lower case) levels (T-tests). Results in (a) have been adjusted against the CO<sub>2</sub>  
752 production observed in blanks ( $n = 2$ ).

753

754 Fig. 5. Effects of dark and alternating treatments on the CO<sub>2</sub> production rate in the wet treatment  
755 during (a) Days 1-64 and (b) Days 65-128 of the short-term photoprimering experiment. Error bars  
756 indicate standard errors of means ( $n = 5$ ). \* indicates statistical differences between treatments at  
757  $\alpha = 0.05$  level (T-tests). Arrows indicate water addition events. Grey panels in the background  
758 represent the dark phase in the alternating treatment. Note the difference in the scale of CO<sub>2</sub>  
759 production between (a) and (b).

760

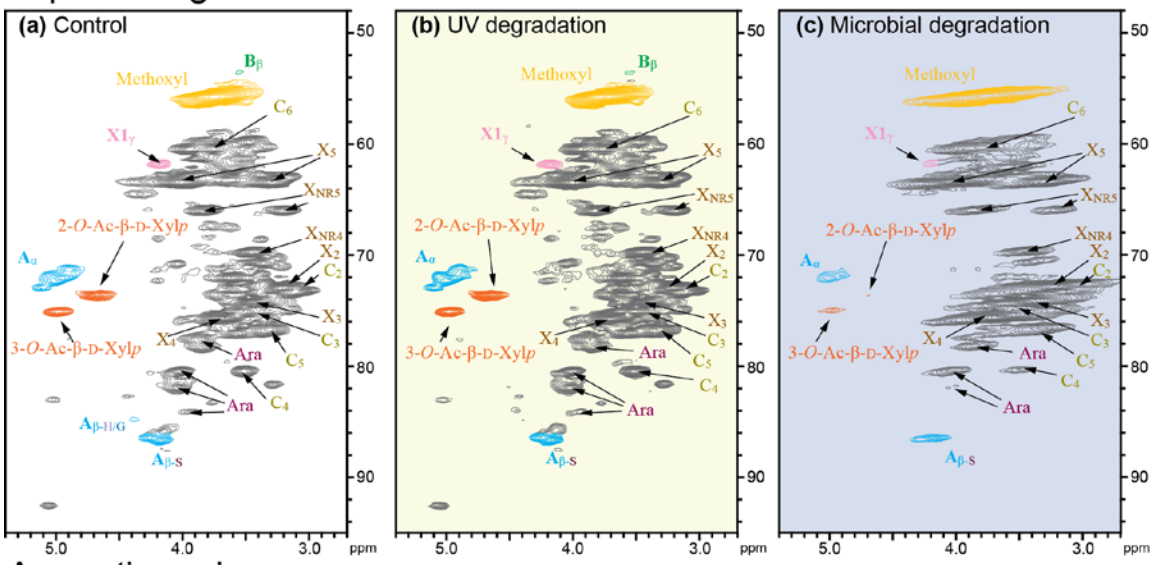
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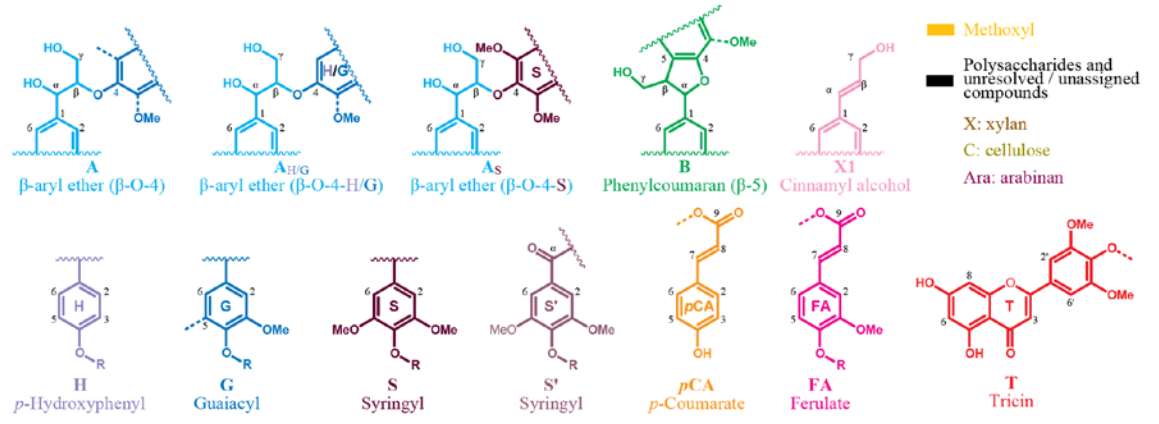
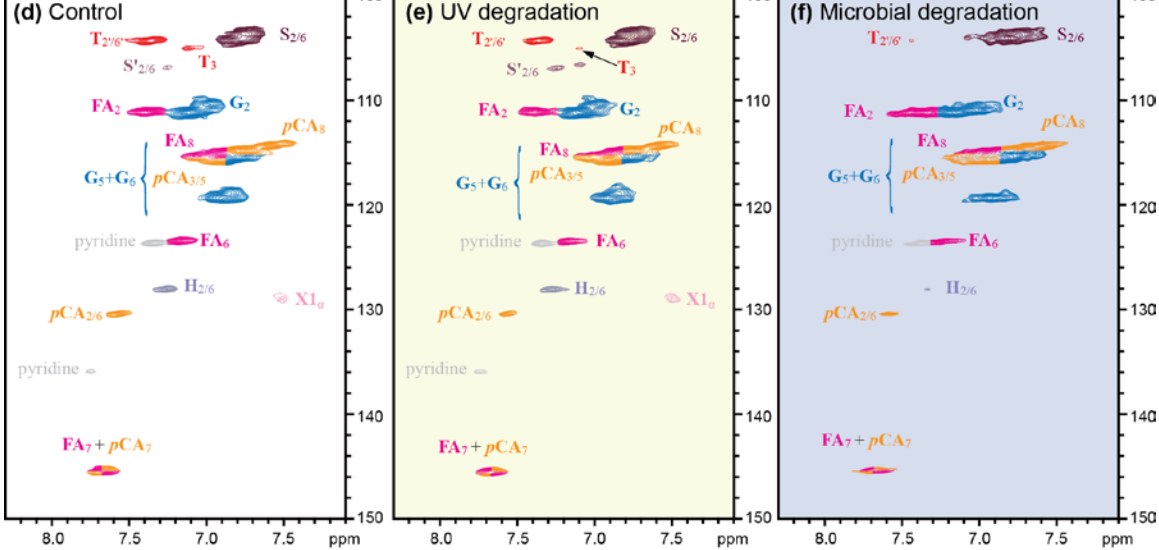
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763 Fig.1

# Aliphatic region



# Aromatic region



764

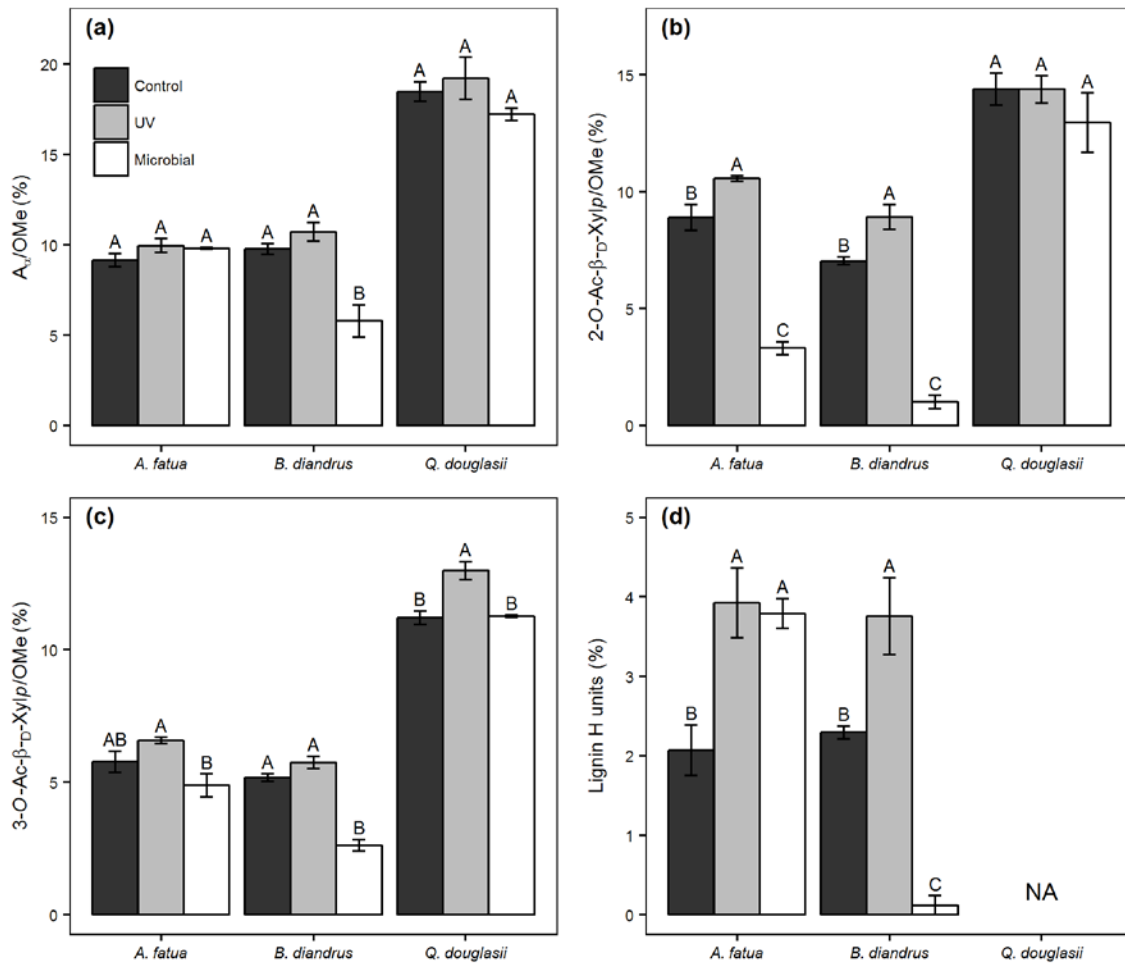
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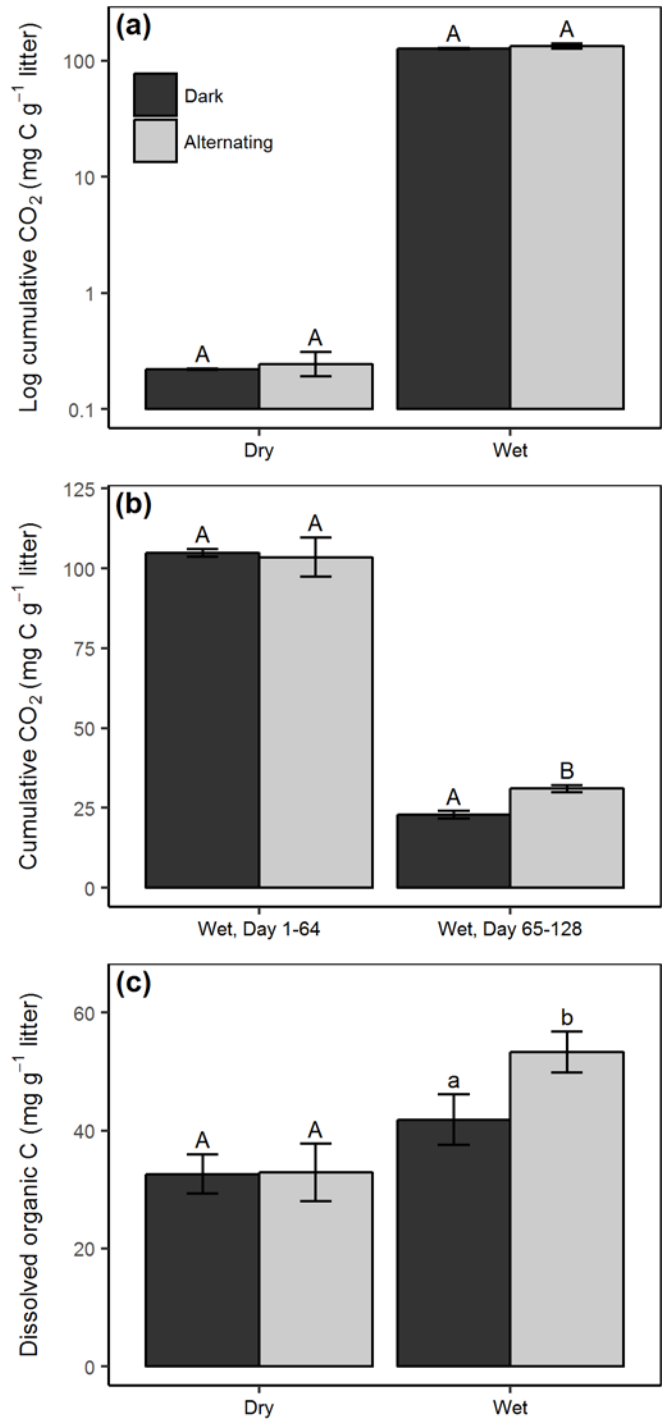
Fig.2

766

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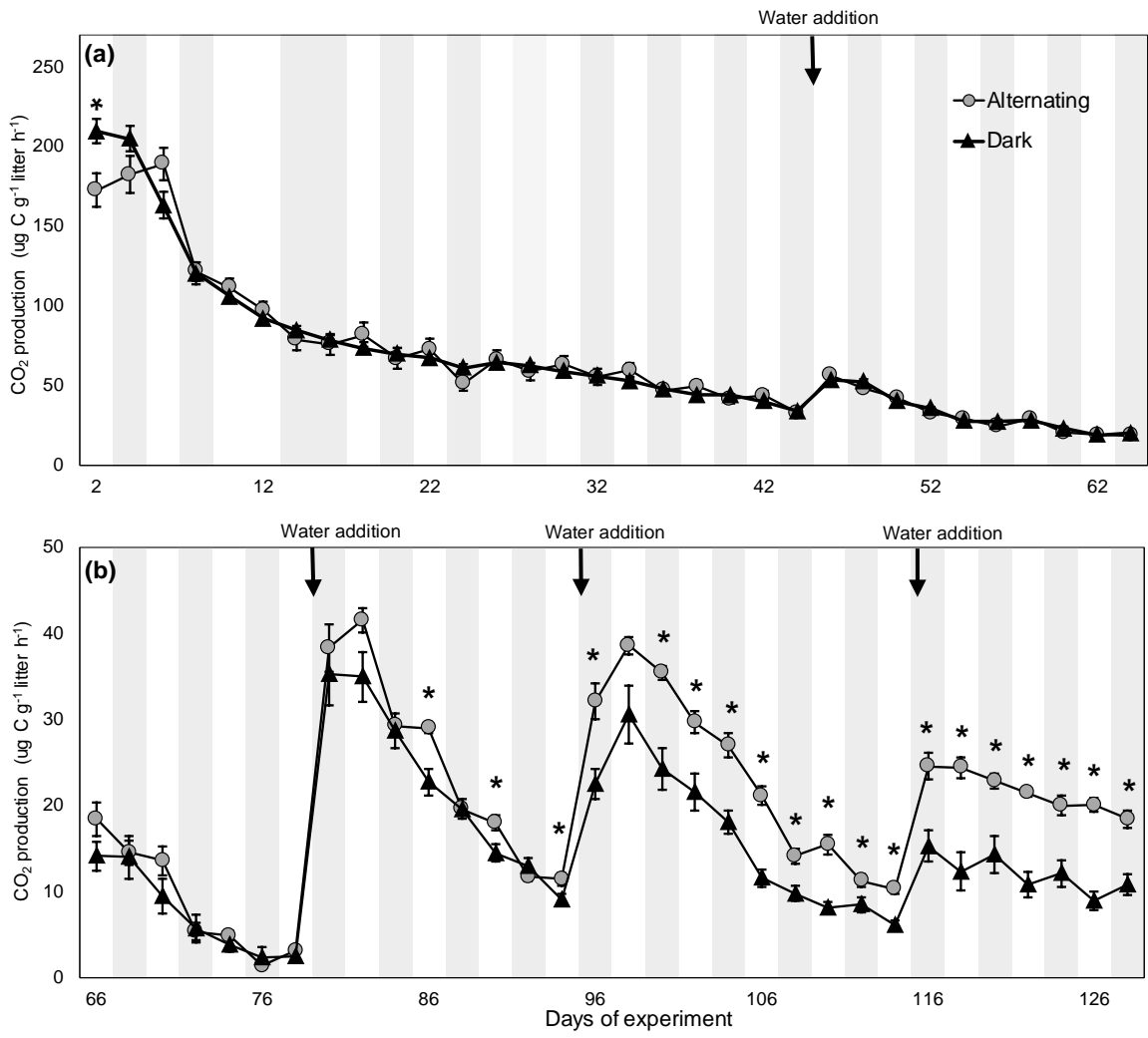






771

772 Fig. 4



773

774 Fig.5

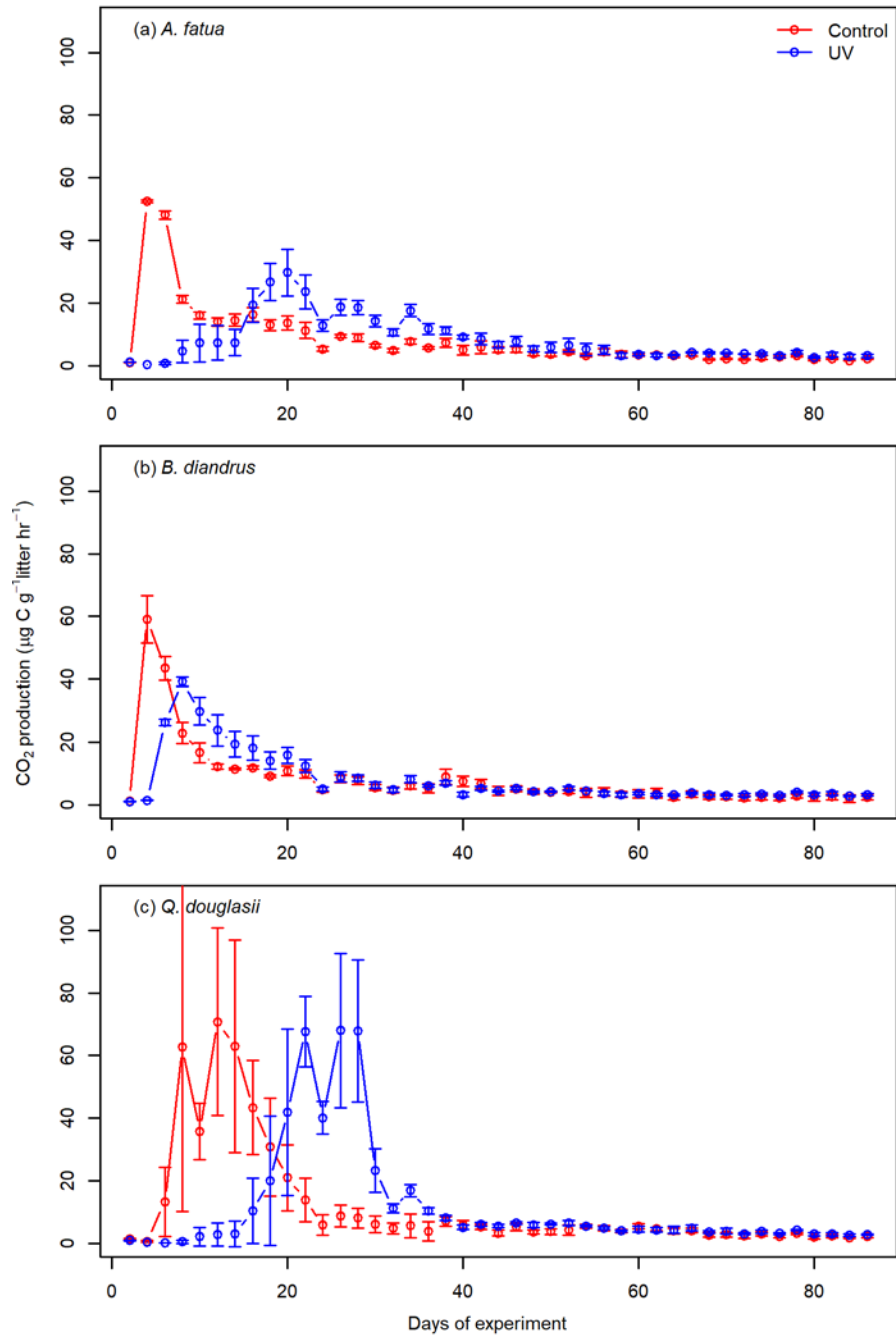


Fig S1. Effects of UV exposure and control treatments on the instantaneous CO<sub>2</sub> production rate of (a) *A. fatua*, (b) *B. diandrus*, and (c) *Q. douglasii* litter during subsequent microbial decomposition. Means and S.E.s are shown.