1 **Shedding light on plant litter decomposition: advances, implications and**

2 **new directions in understanding the role of photodegradation**

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Abstract

Litter decomposition contributes to one of the largest fluxes of carbon (C) in the terrestrial biosphere and is a primary control on nutrient cycling. The inability of models using climate and litter chemistry to predict decomposition in dry environments has stimulated investigation of non-traditional drivers of decomposition, including photodegradation, the abiotic decomposition of organic matter via exposure to solar radiation. Recent work in this developing field shows that photodegradation may substantially influence terrestrial C fluxes, including abiotic production of carbon dioxide, carbon monoxide, and methane, especially in arid and semi-arid regions. Research has also produced contradictory results regarding controls on photodegradation. Here we summarize the state of knowledge about the role of photodegradation in litter decomposition and C cycling and investigate drivers of photodegradation across experiments using a meta-analysis. Overall, increasing litter exposure to solar radiation increased mass loss by 23% with large variation in photodegradation rates among and within ecosystems. This variation was tied to both litter and environmental characteristics. Photodegradation increased with litter C to nitrogen (N) ratio, but not with lignin content, suggesting that we do not yet fully understand the underlying mechanisms. Photodegradation also increased with factors that increased solar radiation exposure (latitude and litter area to mass ratio) and decreased with mean annual precipitation. The impact of photodegradation on C (and potentially N) cycling fundamentally reshapes our thinking of decomposition as a solely biological process and requires that we define the mechanisms driving photodegradation before we can accurately represent photodegradation in global C and N models.

Introduction

Ecosystem carbon (C) and nutrient cycling is driven by the two fundamental processes of production and decomposition. In terrestrial ecosystems, the physical and biological controls on ecosystem productivity are relatively well known and can be accurately modeled (Cramer et al. 1999), but researchers have had less success modeling decomposition rates across space and time, especially of leaf litter on the soil surface (Whitford et al. 1981; Moorhead et al. 1999; Gholz et al. 2000; Adair et al. 2008). Work over the last five years suggests that an abiotic process, photodegradation, may help to explain some of the problems in modeling decomposition to date (e.g. Parton et al. 2007).

Photodegradation, the breakdown of organic matter via solar radiation, can increase decomposition rates and lead to changes in the way C and nutrients are cycled among plants, soil and atmosphere. There are several paths by which solar radiation has been observed to influence pools and fluxes associated with plant litter decomposition (Fig. 1). Solar radiation may increase decomposition fluxes from soil organic matter (SOM) and litter via abiotic photochemical reactions or facilitation of microbial decomposition through the production of labile photodegraded material (e.g. Austin and Vivanco 2006, Brandt et al. 2009, Foereid et al. 2010). However solar radiation can also have negative effects on fluxes through direct negative impacts on microbial and plant growth (e.g. Johanson et al. 1995, Johnson 2003). Thus, solar radiation may decrease pool sizes by suppressing plant growth and associated inputs or by increasing outputs from litter, soil and dissolved organic matter (DOM; via photodegradation/facilitation of decomposition). Solar radiation may increase or decrease the recalcitrance and microbial uptake of DOM depending on the source of DOM (Moran and Zepp 1997). CO_2 fluxes from microbial respiration can be positive or negative depending on whether solar radiation has a net positive effect by increasing labile carbon or a net negative effect by reducing microbial growth (e.g. Foereid et al. 2010, Johnson 2003).

62   Given the complexity of solar radiation effects on decomposition, an increased understanding of the

63   underlying mechanisms is critically needed. Here, we summarize recent advances in understanding the

64   role of photodegradation in plant litter decomposition in three main areas: 1. the mechanisms by which

65   litter is photodegraded; 2. the role photodegradation plays in the global carbon cycle; 3. the factors that

66   influence role of photodegradation in litter mass loss across all field experiments to date using a meta-

67   analysis. We then explore implications for modeling biogeochemical processes. Finally, we provide

68   recommendations for future research needed to fill critical gaps in the understanding of this important

69   process.

70   ## Historical context

71   Research on decomposition has shown that litter in arid ecosystems decomposes faster than predicted

72   by microbial drivers, namely climate and litter chemistry (Whitford et al. 1981; Adair et al. 2008; Austin

73   2011). Several hypotheses for this phenomenon have been proposed, such as litter consumption by

74   termites (Johnson and Whitford 1975; Whitford et al. 1982). Pauli et al. (1964) first proposed that solar

75   radiation may play a role in driving decomposition in arid ecosystems and although the idea was

76   reiterated two decades later (Moorhead and Reynolds 1989), the hypothesis went largely untested with

77   a few exceptions (Zlotin 1979; Mackay et al. 1994).

78   Recognition of the impacts of chlorofluorocarbons on stratospheric ozone in the 1980s led to research

79   on the impacts of increased ultraviolet-B radiation (UV-BR) on decomposition and nutrient cycling

80   (related to the most recent United Nations Environment Programme (UNEP) Environmental Effects

81   Assessment Panel (EEAP) Report, see Ballaré et al. 2011 and Zepp et al. 2011 and references therein).

82   These studies focused primarily on decomposition in high latitude systems where ozone depletion is

83   greatest (Gehrke et al. 1995; Johanson et al. 1995; Paul et al. 1999). Many of these studies indicated that

84   the primary mechanisms of UV-BR impacts on decomposition were indirect, mediated through changes

85   in litter chemistry or changes in soil biota, rather than the direct result of incident UV-BR inducing litter

86   mass loss (reviewed in Paul et al. 1999). These studies provided important advances in methodology for

87   manipulating solar radiation at different wavelengths and introduced the concept of photodegradation

88   to a larger audience in the terrestrial ecology field.

89   Research on the contribution of plants and litter to atmospheric trace gas concentrations became a

90   topic of interest in the 1990s and remains so today. Work in the 1990s on carbon monoxide (CO)

91   emissions showed that solar radiation plays a large role in CO emissions from plant litter and SOM (Tarr

92   et al. 1995; Schade et al. 1999; Kisselle et al. 2002). However, the role of solar radiation in the

93   production of other trace gases from plants, litter and soil remained largely ignored until the past five

94   years. One exception was work by Anesio et al. (1999), showing that carbon dioxide (CO_2) could also be

95   produced by photodegradation.

96   In contrast to terrestrial systems, work in the 1990s on biogeochemical cycling in aquatic systems

97   significantly advanced understanding of photodegradation's role in decomposing DOM. The large body

98   of work in marine and freshwater systems indicates that photochemical reactions with DOM produce an

99   additional 1 Gt C yr^{-1} and 15 Mt nitrogen (N) yr^{-1} for heterotrophic utilization and convert 12-16 Gt C yr^{-1}

100   to CO_2 through direct photochemical reactions (Moran and Zepp 1997). Research on DOM continues to

101   explore variation among and within systems in photodegradation rates (e.g., with changes in salinity,

102   DOM source and temperature) and interactions with microbial utilization (Obernosterer and Benner

103   2004; Anesio et al. 2005; Amado et al. 2007; Nelson et al. 2010). Recent work has focused on identifying

104   underlying mechanisms of DOM photochemical reactions (Boreen et al. 2008; Cory et al. 2010; Vione et

105   al. 2010). Other studies have examined photodegradation of submerged or emergent aquatic

106   vegetation, providing a link between terrestrial litter decomposition and aquatic systems (Denward and

107   Tranvik 1998; Vähätalo et al. 1998; Anesio et al. 1999; Denward et al. 2001).

108 As questions remained about the relatively high rates of litter decomposition in arid ecosystems,

109 terrestrial ecologists, informed by the findings and methods from aquatic systems, began to investigate

110 the potential importance of photodegradation.

Mechanisms

111

112 How does exposure to solar radiation degrade terrestrial litter and soil? The mechanisms involved, and

113 whether they are similar to those discovered in the fields of aquatic biochemistry, materials science and

114 atmospheric chemistry, remain relatively unknown. Here we discuss our current understanding of the

115 mechanisms underlying litter mass loss through photodegradation, as well as possible mechanisms

116 gleaned from work in other fields.

Wavelength

117

118 It was originally hypothesized that wavelengths in the UV-B range (280-320 nm) were responsible for

119 photodegradation, but sufficient evidence suggests that other wavelengths, particularly those in the UV-

120 A range (320-400 nm) and the short-wave visible range (400-500 nm), play an equal if not greater role

121 (Austin and Vivanco 2006; Brandt et al. 2009; Austin and Ballaré 2010). Many plant compounds have a

122 maximum absorbance in the UV-B range, but they also absorb lesser amounts of radiation at other

123 wavelengths. Since the atmosphere absorbs much of the UV-BR before it hits Earth's surface, visible

124 and, to a lesser extent, UV-A radiation make up a much larger proportion of the photon flux to the litter

125 layer. Therefore, litter photodegradation rates may be higher on a *per photon* basis in the UV-B range,

126 but lower *in total* compared to longer wavelengths. Such hypotheses have yet to be tested (Box 1,

127 "Mechanistic research"), but recent work has pushed forward our understanding of terrestrial

128 photodegradation by expanding the definition of photo-active radiation to include shortwave visible

129 wavelengths.

Photoreactive compounds

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131   It has long been assumed that lignin is the primary compound in litter susceptible to photodegradation,

132   but there has been relatively little evidence to support this assumption. Studies that have measured

133   changes in litter chemistry over time under different radiation treatments have typically found only

134   small treatment effects on either lignin or other compounds such as cellulose (Rozema et al. 1997;

135   Brandt et al. 2007; Day et al. 2007; Brandt et al. 2010). However, a recent study by Austin and Ballaré

136   (2010) showed that photodegradation did not occur when lignin-free, pure cellulose substrates were

137   exposed to radiation but did occur when a lignin solution was added to the substrates. Furthermore,

138   rates of photodegradation increased with solution lignin concentration, and mass loss patterns were

139   consistent with what would be predicted if only lignin were lost in this process. This study shows that

140   lignin is at least one of the photoreactive compounds and that cellulose (in a highly purified form) does

141   not appear capable of absorbing radiation and photodegrading in isolation. This study only tested two

142   highly purified forms of lignin and cellulose. Results could vary with plant species differences in lignin

143   structure and chemistry and the extent of decomposition that has already occurred. Lignin in the

144   lignocellulose matrix of plant tissue may have a different susceptibility to photodegradation than

145   purified lignin. It is also possible that compounds not examined in this study could be photoreactive,

146   including proteins and other phenolics besides lignin (see Box 1).

147   **Direct and indirect photolysis**

148   The chemical mechanisms behind litter photodegradation remain unknown, but general principles of

149   photochemistry along with evidence from other fields can provide a good starting point. When a

150   molecule absorbs radiation and it results in a permanent change to the molecule, such as fragmentation,

151   intramolecular rearrangement or electron transfer from or to the molecule, it is generally referred to as

152   "direct photolysis" (Fig. 5). For example, a lignin molecule could undergo fragmentation into smaller

153   organic components, which then could be consumed by microbes or leached out of the litter layer. This

154   fragmentation could also result in the formation of inorganic C compounds such as CO or CO_2. Research

155   on photodegradation of DOM in aquatic systems has shown that direct photolysis does occur to some

156   extent (Kieber et al. 1999). This mechanism may be a factor in studies that have shown a decrease in

157   litter lignin content when exposed to solar radiation (Rozema et al. 1997, Day et al. 2007, Henry et al.

158   2008, Austin and Ballaré 2010).

159   In addition to direct photolysis, "indirect photolysis" may also play a role in the decomposition of

160   organic substrates (Fig. 5; see also review by Lanzalunga and Bietti 2000). During indirect photolysis,

161   photosensitizers absorb radiation and transfer energy to other molecules (often triplet oxygen), creating

162   reactive intermediates such as singlet oxygen, hydroxyl radical or hydrogen peroxide. Other important

163   reactive intermediates can include reduced iron, copper or manganese. Reactive intermediates then

164   change the chemistry of another non-light-absorbing molecule or part of the same molecule where the

165   photosensitizer resided. In the case of litter photodegradation, light-absorbing (chromophoric)

166   structures in lignin or molecules in litter may act as photosensitizers, facilitating chemical

167   transformations of compounds that do not absorb much radiation, such as non-chromophoric lignin

168   components, cellulose or hemicellulose. Research in aquatic systems and on wood and paper materials

169   has shown that indirect photochemical processes are the primary mechanisms by which many organic

170   materials are photodegraded (reviewed in George et al. 2005; Cory et al. 2010). In addition, recent

171   studies have shown that photosensitized production of reactive oxygen species is the primary

172   mechanism for photochemical production of CH_4 from plant pectins (McLeod et al. 2008, Messenger et

173   al. 2009). This mechanism could explain why some studies have seen decreases in cellulose but not

174   lignin when litter is exposed solar radiation (Brandt et al. 2007; Brandt et al. 2010). Indirect photolysis

175   could be an alternative mechanism for observed lignin loss (Rozema et al. 1997; Day et al. 2007; Henry

176   et al. 2008; Austin and Ballaré 2010). In addition, direct photolysis may also result in the production of

177   reactive intermediates that can facilitate indirect photolysis (Lanzalunga and Bietti 2000).

Interactions with other decomposition processes

Modifications to litter by direct or indirect photochemical processes can lead to modifications in other decomposition processes, including the biodegradability of litter. A recent study showed that pre-exposure of litter to solar radiation can make it more digestible when subsequently decomposed under conditions favoring microbial decomposition (Foereid et al. 2010). Another recent study suggests that the radiation exposure conditions for plant litter may affect the size of respiration pulses of CO_2 emissions during subsequent precipitation events (Ma et al. 2012). The facilitation of microbial decomposition by photodegradation appears to depend heavily on length of exposure, and studies exposing litter for short periods of time (e.g. a season) do not show the same effects as those conducted over longer time periods (Brandt et al. 2009; Foereid et al. 2010; Kirschbaum et al. 2011). However, studies in the aquatic literature have shown that photodegradation effects on subsequent microbial decomposition can also be negative, depending on the chemistry of organic materials being bio-and photo-degraded (Tranvik and Bertilsson 2001). Since relatively few studies have examined this interaction, it is too early to generalize about the magnitude or direction of this interaction.

Photodegradation can also interact with other physical decomposition processes. It can increase the solubility of litter, leading to increased leaching (Gallo et al. 2006; Feng et al. 2011). Research by Feng et al. (2011) suggests that this effect may be dependent on litter type, as increases in water-extractable organic C from photodegradation were seen for pine but not maize litter. This may explain why a study examining grass and oak litters found no effect of UV-radiation exposure on DOC leached from litter (Brandt et al. 2009), while another study examining conifer litter reported a significant increase (Gallo et al. 2006). In addition to leaching, physical processes common in arid, light-exposed systems such as wind or soil abrasion could interact with photodegradation, but this interaction remains relatively unstudied (Throop and Archer 2007; Austin 2011). One recent study suggests that freeze-thaw cycles in colder climates may contribute to accelerated mass loss by photodegradation (Uselman et al. 2011).

Influence on the Global Carbon Cycle

The effects of ozone depletion and climate change on ultraviolet radiation are expected to have measurable impacts on the global C cycle (Zepp et al. 2011), but the specific contributions of photodegradation are not well known. The factors that affect solar radiation exposure and, therefore, photodegradation, are highly complex, varying considerably with ecosystem type, as well as through space and time (Table 1). Foereid et al. (2011) estimated of the importance of photodegradation to overall litter decomposition on a global scale by comparing modeled global photodegradation fluxes, based on experimental data from three sites, against ecosystem NPP. Their modeled estimates suggest that only 0.5 to 1.6% of global NPP is photodegraded. However, in dry, light-exposed ecosystems, up to 14% of NPP can be lost via photodegradation (Foereid et al. 2011). It appears that the primary influence of photodegradation on the C cycle is to accelerate return of C to the atmosphere. Well-documented pathways of C return to the atmosphere are the direct abiotic losses of CO_2 (Anesio et al. 1999; Brandt et al. 2009; Rutledge et al. 2010), CO (Tarr et al. 1995; Schade et al. 1999; Kisselle et al. 2002; Derendorp et al. 2011b), methane (CH_4, McLeod et al. 2008; Vigano et al. 2008; Bruhn et al. 2009; Messenger et al. 2009) and trace amounts of ethane and ethylene and other hydrocarbons (McLeod et al. 2008; Derendorp et al. 2011a; Table 2).

The first estimates of photochemical CO_2 emissions were based on exposure of dry aquatic macrophyte litter to only UV radiation in the laboratory (0.0108 g C m^{-2} d^{-1}; Anesio et al. 1999). In comparison, measurements made in microcosms under natural solar radiation on clear sunny days in summer resulted in slightly higher estimates (0.016 g C m^{-2} d^{-1}) and showed that other wavelengths play a role in litter photodegradation (Brandt et al. 2009). Rutledge et al. (2010) estimated photodegradation CO_2 emissions based on eddy covariance and clear chamber measurements during daylight and non-daylight hours. Their estimates (0.186 g C m^{-2} d^{-1} in annual grasslands during the dry season and 0.093–0.18 g C m^{-2} d^{-1} in harvested peatlands) are much higher than the laboratory and microcosm measurements

226   described above. Such contrasting estimates make it clear that a better understanding of how and why

227   rates of photochemical CO_2 production vary across ecosystems (e.g., variation in radiation exposure;

228   Table 1) is needed before we can make accurate estimates of its contribution to global CO_2 emissions.

229   Measured rates of photochemical CO production from litter under natural or simulated solar radiation

230   conditions generally range from approximately 2 to 5.5 mg C m^{-2} d^{-1} (Tarr et al. 1995; Schade et al. 1999;

231   Kisselle et al. 2002; Table 2). Using response factors developed for CO emissions together with global

232   land area and irradiance datasets, Schade and Crutzen (1999) estimated the global source strength of

233   CO emissions from photodegradation to be on the order of 100 Tg CO y^{-1}. Schade et al. (1999) also

234   measured thermal emissions of CO, but those emissions were lower, by as much as an order of

235   magnitude, than photochemical emissions. In a recent study, Lee et al. (2012) documented the

236   production of CO, as well as CO_2 and CH_4, through photodegradation and thermal processes. Their

237   controlled laboratory study of six different plant materials showed that higher production of trace gases

238   occurred during photodegradation compared to thermal degradation and that photodegradation

239   production rates varied depending on temperature. The molar ratio of thermal degradation to

240   photodegradation for CO ranged from 0.07 to 0.28 (for temperatures from 25°C to 55°C; Lee et al.

241   2012). This result is similar to the findings of Schade et al. (1999). Consistent with our summary of trace

242   gas production in separate studies (Table 2), Lee et al. found, using simultaneous measurements of

243   these trace gases, that the primary trace gas produced during both photodegradation and thermal

244   degradation is CO_2 (Lee et al. 2012).

245   The magnitude of photochemical CH_4 fluxes varies depending on experimental conditions and on

246   materials exposed (Table 2; values in Table 2 converted to ng C g dry $weight^{-1}$ h^{-1} for comparison). Most

247   studies to date have focused on a limited set of plant materials (tobacco leaves, citrus pectin) or plant

248   structural compounds (lignin, pectin, but see Lee et al. 2012). McLeod et al. (2008) reported CH_4

249   emissions of up to 661 ng CH_4 g dry weight^{-1} h^{-1} for citrus pectin, while Bruhn et al. (2009) reported

250   emissions that ranged from 5-17 ng CH_4 g dry weight^{-1} h^{-1} for similar material. The widest range of

251   materials studied is reported by Vigano et al. (2008) in which the range of CH_4 emissions was also wide

252   (0-4300 ng CH_4 g dry weight^{-1} h^{-1}). Bloom et al. (2010) used an approach similar to Schade and Crutzen

253   (1999) to estimate global CH_4 emissions derived from photodegradation of foliar pectin. Their estimate,

254   0.2–1.0 Tg CH_4 y^{-1}, is small compared to other estimates of foliar CH_4 emissions (1-7 Tg CH_4 y^{-1}, Keppler

255   et al. 2006) and points to the need for further mechanistic studies (Box 1).

256   Little is known about the influence of photodegradation on other biogeochemical cycles, such as

257   nitrogen (N). Because photodegradation is an abiotic process, litter that is low in N and is primarily

258   decomposed by photodegradation should not have the same immobilization and mineralization patterns

259   that are often observed in systems controlled by microbial decomposition (Parton et al. 2007). A few

260   studies have found partial support for this hypothesis (Brandt et al. 2007; Smith et al. 2010). In addition,

261   a study by McCalley and Sparks (2009) showed that soil exposed to solar radiation releases trace N gases

262   at higher rates than when kept under dark conditions, and Mayer et al. (2012) recently reported N

263   release with photodissolution of soil organic matter. This suggests that, as with C, photodegradation

264   speeds up N losses to the atmosphere and reduces N storage in litter and soil organic matter.

Effects on litter mass loss: a meta-analysis

266   What factors across ecosystems influence the role photodegradation plays in litter decomposition? Field

267   researchers have attempted to quantify the role of photodegradation in litter decomposition by

268   manipulating the amount of solar radiation reaching the litter layer and measuring litter mass loss over

269   time. Most field studies examine the effect of photodegradation in the presence of microbial

270   decomposition (but see Austin and Vivanco 2006). The photodegradation effect is thus the difference in

271   mass loss or decay rates between a control (e.g., that allows all radiation to pass through) and a

272 treatment that either reduces solar radiation by filtering photodegradative wavelengths (UV-B, UV-A,

273 and/or other wavelengths), blocking radiation completely, or increasing UV-BR using lamps. To examine

274 the magnitude of solar radiation effects on mass loss (ML), we built a data set consisting of 50 field

275 experiments drawn from 16 published, peer-reviewed sources (Appendix A; through July of 2011). We

276 tested the influence of different treatment combinations, experimental approaches, initial lignin

277 content, litter C to N ratio (C/N) and litter area to mass ratio (area/mass) for the log response ratio for

278 final mass loss (ML) of the higher solar radiation treatment compared to the lower solar radiation

279 treatment for all studies (LRR$_{enh}$, see Appendix A for more details).

280 ***Effects of Radiation Treatment and Experimental Methods***

281 Higher exposure of litter to solar radiation increased ML by 23% on average across all studies (Fig. 2a);

282 however, results varied in relation to the type of experimental treatment. The experiments that

283 compared enhanced UV-BR to reduced or ambient UV-BR found that increasing exposure had no effect

284 on ML (95% CI included zero), although these results may change with a larger sample size. Often, such

285 experiments were designed to investigate the role of ozone depletion and the resulting increases in UV-

286 BR on plant growth and litter chemistry, and thus only manipulated UV-B wavelengths by dosage

287 changes projected to occur with ozone thinning. In these experiments, UV-BR-induced changes in litter

288 quality also failed to impact photodegradation (95% CI encompassed zero for litter produced under

289 ambient, N=10, and enhanced, N=4, radiation; data not shown). In contrast, mass loss consistently

290 increased in experiments that compared litter exposed to ambient versus reduced UV-BR, UV-A+BR, or

291 total solar radiation (32% on average; LRR$_{enh}$ > 1; Fig. 2a). These experiments were more often designed

292 specifically for testing the hypothesis that photodegradation played a role in litter mass loss in systems

293 with high levels of radiation exposure and low moisture availability, and thus compared ambient

294 controls to treatments that blocked a certain wavelength entirely.

295 Methods used to impose radiation treatments also affected the ML response, but it is difficult to tease

296 apart the effect of method from the effect of experimental treatment (above). Enhancing litter exposure

297 to UV-BR via supplementary lamps had no effect on ML (N=14, 95% CI included zero; Fig. 2b). To date,

298 no other methods have been used to increase the exposure of litter to UV-BR to examine effects on ML.

299 Using shade cloths or filter treatments to reduce total solar radiation or UV radiation (UVR) reduced ML

300 by 45% and 25%, respectively (n = 11 and 25, respectively; Fig. 2b).

301 In studies that reduced solar radiation, reducing only UV-BR had the smallest effect on ML (95% CI

302 included zero; Fig. 2c). In contrast, blocking all solar radiation (via shade), radiation with wavelengths <

303 450 nm, or UVA+BR all increased ML (Fig. 2c). Evidence to date suggests that short wavelength radiation

304 in the visible range (400-500 nm) may substantially increase photodegradation (Fig. 2c; Brandt et al.

305 2009). However, this study has yet to be replicated, so the magnitude of this effect is uncertain.

Influence of Radiation Exposure

307 The amount of radiation to which litter is exposed can be influenced by a variety of environmental

308 factors including latitude, elevation, canopy cover and cloud cover, leading to increases or decreases in

309 photodegradation rates (Table 1). It is difficult to tease apart the relative influence of these factors on

310 photodegradation rates because the number of studies is limited, studies often use slightly different

311 experimental approaches (see above), and many of these factors tend to co-vary. In general, our meta-

312 analysis suggests that studies conducted at mid-latitude arid sites with low canopy cover demonstrate

313 larger photodegradation effects compared to higher latitude sites, which could be due in part to greater

314 radiation dosage at mid-latitude arid sites (LRR_{enh} decreased with increasing latitude in field experiments

315 that compared ambient to reduced solar radiation; Fig 3a). This effect was independent of method

316 (shade or filter) or wavelengths excluded (e.g., UV-B or UV-A+B; data not shown).

317   Not examined in the meta-analysis (due to lack of sufficient data) are the effects of other factors on

318   radiation exposure (Table 1). For example, Brandt et al. (2010) conducted a field study comparing

319   photodegradation rates in three contrasting grassland systems, hypothesizing that photodegradation

320   rates should increase with decreasing latitude and increasing aridity. However, they found that factors

321   such as seasonal monsoons and soil burial decreased the influence of photodegradation in the most arid

322   site. Other studies have shown that burial by soil or additional litter can reduce exposure to radiation

323   and thus reduce photodegradation rates (Henry et al. 2008; Throop and Archer 2009; Barnes et al.

324   2011).

325   *Influence of Precipitation*

326   Our meta-analysis suggests that photodegradation plays the largest role in dry environments. With one

327   exception, the LRR_{enh} decreased with mean annual precipitation (MAP; Fig 3b). Precipitation data were

328   only available for experiments that compared ambient to reduced solar radiation, so it is not known if

329   this relationship would be significant for experiments that enhanced UV-BR. The exception to this trend

330   was a single photodegradation study conducted in a Mediterranean climate (Henry et al. 2008). This site

331   had both high MAP and photodegradation rates (Fig. 3b; Appendix A). The large effect of increasing litter

332   exposure to solar radiation was likely due to the highly seasonal nature of rainfall, which began several

333   months after litter was placed in the field. This result suggests that MAP may not be a good predictor of

334   photodegradation in climates with highly seasonal rainfall patterns.

335   A few studies have directly examined the influence of precipitation or moisture on the relative

336   importance of photodegradation (Brandt et al. 2007; Gallo et al. 2009; Smith et al. 2010). These studies

337   tested the hypothesis that under dry conditions, photodegradation should be more easily detectable,

338   while under wet conditions microbial decomposition should dominate, not because photodegradation is

339   reduced under wet conditions, but rather because microbial decomposition is reduced by dry

340   conditions, making the photodegradation signal clearer. In addition, these studies hypothesized that

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341   under wet conditions, overall decomposition rates would decrease when litter is exposed to radiation

342   because of negative impacts of UV-BR on the microbial community (Moody et al. 1999; Pancotto et al.

343   2003). In general, findings support these hypotheses (Brandt et al. 2007; Smith et al. 2010). However,

344   one study conducted in a riparian forest in New Mexico did not find a precipitation effect, which the

345   authors attributed to a low (15%) difference between the precipitation treatment and control (Gallo et

346   al. 2009). It is important to note that photochemical reactions could potentially be moisture-dependent

347   (Schade et al. 1999) or could lead to increased litter solubility (Gallo et al. 2006), so actual

348   photodegradation rates may be lower under dry conditions despite the fact that it accounts for a larger

349   proportion of litter mass loss in dry versus mesic environments.

Influence of Litter Characteristics

351   Because lignin has been identified as a photosensitive compound (George et al. 2005),

352   photodegradation is generally hypothesized to increase with lignin content (e.g. Moorhead and

353   Callaghan 1994; Austin and Ballaré 2010). Instead, we found no relationship between LRR_{enh} and initial

354   lignin content for experiments that compared ambient to reduced solar radiation, and LRR_{enh} actually

355   decreased with increased initial lignin content in experiments that compared enhanced UV to ambient

356   or reduced UV treatments (Fig 4a). The lack of relationship between LRR_{enh} and lignin content may be

357   accurate, but it could also be a consequence of the narrow range of lignin contents used in reduced

358   solar radiation experiments thus far (Fig. 4a; the one exception is Day et al. 2007 with a lignin content of

359   ~ 32%). However, LRR_{enh} did increase with initial litter C/N (Fig. 4b). An increase in litter C/N can reduce

360   microbial decomposition rates because of low N availability, thus increasing the proportion of

361   decomposition that is due to photodegradation. LRR_{enh} was also positively related to litter area/mass

362   (Fig. 4c), a relationship that held across all reduced radiation experiments regardless of method or

363   wavelengths excluded (data not shown; Appendix A). This suggests an influence of litter density,

364   presumably due to the shading of bottom litter layers from radiation by top layers in low area/mass

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365 experiments. Brandt et al. (2009) found support for this hypothesis by demonstrating that increasing

366 litter density decreased photochemically-derived CO_2 on a per unit mass basis, while CO_2 released per

367 unit area remained constant.

368 In addition to lignin content and litter density, other chemical and physical properties of litter could

369 potentially influence photodegradation rates, but have not yet been examined. Studies in aquatic

370 systems have shown that iron (Fe^{3+}) can play a large role in photodegradation of dissolved organic

371 matter (DOM; Gao and Zepp 1998); thus litter iron content may be an important factor. Other studies of

372 DOM have shown that the degree to which DOM has been biodegraded can affect subsequent

373 photodegradation rates and vice versa (Obernosterer and Benner 2004), so this may also hold true for

374 litter. Other radiation-absorbing compounds such as flavonoids, tannins and anthocyanins may also

375 influence photodegradation but have remained unexamined. Physical characteristics such as the

376 presence of trichomes or cutin on the leaf surface may affect photodegradation rates by preventing

377 radiation transmission. Many plants in arid environments have these characteristics to (at least in part)

378 protect themselves from solar radiation, so these physical characteristics should be addressed when

379 attempting to estimate photodegradation rates in arid systems.

380 *Methodological considerations*

381 Some of the variation in the meta-analysis results likely stems from the wide range of methods used to

382 quantify litter photodegradation. Only a few studies have attempted to quantify photodegradation in

383 the absence of microbial activity (Austin and Vivanco 2006; Brandt et al. 2009), and it is unclear whether

384 the methods used may affect photodegradation measurements. Sterilization techniques such as

385 autoclaving or gamma irradiation may change litter chemistry as it does for SOM chemistry (e.g. Kelsey

386 et al. 2010), and chemical biocides may interfere with or promote photochemical reactions in the litter

387 (Katagi 2004). Finally, eliminating the microbial component may under- or overestimate the total

388 contribution of photodegradation to decomposition by eliminating the potential positive or negative

389   effects that photodegradation may have on subsequent microbial decomposition (Henry et al. 2008;

390   Gallo et al. 2009; Foereid et al. 2010). Thus, most field studies have examined the effect of

391   photodegradation in the presence of microbial decomposition by placing unaltered litter in the field.

392   Another factor that may contribute to variation among studies is the method used to contain litter.

393   Many studies have used the standard litterbag technique with either supplementary UV-B lamps

394   (Gehrke et al. 1995; Newsham et al. 1997; Moody et al. 2001), filters (Pancotto et al. 2003; Pancotto et

395   al. 2005; Brandt et al. 2007; Brandt et al. 2010), or shade cloths (Mackay et al. 1994; Köchy and Wilson

396   1997; Gallo et al. 2009) to manipulate the amount of radiation reaching the litterbag. The use of lamps

397   or filters above traditional litterbags has the advantage of being directly comparable to other litterbag

398   studies. This technique also has relatively minor effects on microclimate because filters and lamps are

399   not in contact with the litter and can have perforations large enough to allow precipitation to reach the

400   litter layer. In addition, filters and lamps can be replaced periodically to ensure consistent UV

401   treatments. The disadvantage is that the mesh used in constructing litterbags covers a substantial

402   proportion of the litter (50% for fiberglass and 30% for aluminum), which leads to an underestimate of

403   the effects of solar radiation (either positive or negative).

404   A few studies have constructed litter "boxes" or "packets" with clear UV-transparent or UV-blocking

405   tops and bottoms made out of mesh or UV transparent material (Austin and Vivanco 2006; Day et al.

406   2007; Austin and Ballaré 2010), minimizing the problem of obstructing solar radiation. However, the UV-

407   transparent materials themselves can photodegrade, thus altering their radiation transmission

408   properties over time (Spartech Polycast, personal communication). The materials can also have

409   significant effects on microclimate when placed directly above the litter, increasing temperature and

410   decreasing the amount of precipitation reaching the litter. These factors could potentially lead to an

411   overestimate of photodegradation rates if reaction rates are temperature-dependent or an

412   underestimate of microbial decomposition processes due to low levels of water availability and very

413   high temperatures. Since no method is without problems, we recommend that researchers fully disclose

414   the limitations of their treatments to inform comparisons among studies.

Modeling Photodegradation

416   Now that a basic understanding of the role of photodegradation in litter decomposition and C cycling is

417   emerging, how can this information be incorporated into models of decomposition and biogeochemical

418   cycling? Traditional decomposition models based on biotic drivers of decomposition (i.e., climate and

419   litter chemistry) do not accurately predict decomposition in semi-arid and arid ecosystems

420   (Meentemeyer 1978; Parton et al. 2007; see also Throop and Archer 2009), in some cases under-

421   predicting long-term decomposition by as much as 25% (Adair et al. 2008). A primary candidate for

422   explaining this discrepancy is photodegradation (Austin and Vivanco 2006; Adair et al. 2008; Vanderbilt

423   et al. 2008). Despite this, photodegradation has yet to be adequately incorporated into terrestrial

424   ecosystem models, a failure that is likely due to incomplete understanding of this process.

425   Large unanswered questions remain regarding the mechanisms driving photodegradation, substrate(s)

426   and product(s) of photodegradation, and interactions of photodegradation with climate, local

427   environmental conditions and biotic decomposition. Thus, the four existing terrestrial photodegradation

428   models consist of exploratory exercises (Moorhead and Callaghan 1994; Rozema et al. 1999) or simple

429   attempts to scale up CO production (Schade and Crutzen 1999) and mass loss (Foereid et al. 2011) rates.

430   However, even these few modeling efforts have increased understanding of how photodegradation may

431   fit into ecosystem functioning and large-scale C cycling. Moorhead and Callaghan (1994) modified the

432   CENTURY ecosystem model to account for litter photodegradation by increasing the C transfer rate from

433   structural litter to recalcitrant SOM and adding a C transfer from structural litter to labile SOM. These

434   modifications increased litter turnover rates, but had little effect on SOM dynamics (Moorhead and

435   Callaghan 1994). Another exploratory model allowed exposure to UV-BR to increase litter mass loss (all

436   fractions) and increase the lignin content of litter inputs (due to exposure during growth; Rozema et al.

437   1999). While increasing UV-BR exposure did increase mass loss, UV-BR-induced lignin increases had

438   larger negative effects on mass loss, resulting in slower mass loss rates regardless of UV exposure level

439   (Rozema et al. 1999). However, while many studies have demonstrated that UVR exposure during

440   growth affects plant tissue chemistry (see review in Caldwell et al. 2003), empirical studies have shown

441   that the effects of UV-BR exposure during plant growth on decomposition may be minor or non-existent

442   (e.g. Hoorens et al. 2004). Schade and Crutzen (1999) and Foereid et al. (2011) used models to scale up

443   local photoproduction or photodegradation rates to global levels. Both estimated that

444   photodegradation contributions to global fluxes of CO (Schade and Crutzen 1999) and litter mass loss

445   (Foereid et al. 2011) were relatively small. Such models are useful at a coarse scale, but developing a

446   model that fully accounts for the role of photodegradation in ecosystem function or the global C cycle

447   requires greater understanding of the underlying mechanisms of photodegradation, its substrates and

448   products, as well as its interactions with climate and microbial decomposition (Fig. 6).

449   A substantial challenge for modeling litter photodegradation lies in determining what is being

450   photodegraded. Decomposition models often divide litter into different pools that decompose at

451   different rates (e.g., fast, slow cellulosic and very slow lignin pools; Adair et al. 2008). If only lignin is

452   photodegraded, incorporating photodegradation into traditional pool based models could significantly

453   alter mass loss predictions (as in Moorhead and Callaghan 1994). Currently, there is substantial

454   contradictory evidence as to whether (or how) photodegradation differentially affects various litter

455   compounds or litter types (e.g., Brandt et al. 2009; Austin and Ballaré 2010). It is therefore unclear how

456   to best represent litter mass loss in photodegradation models. While Moorhead and Callaghan (1994)

457   assumed that only lignin was photodegraded, the remaining three studies modeled either litter mass

458   losses without specifying which components were lost (Rozema et al. 1999; Foereid et al. 2011) or

459   product formation without accounting for mass loss (Schade and Crutzen 1999).

460   If photodegradation affects all litter types similarly (if, e.g., mass loss is a function of surface area or

461   there is a universal action spectrum for litter photodegradation), then differences in litter quality (e.g.,

462   lignin content) will not affect photodegradation rates. However, this seems unlikely given findings that

463   DOM photodegradation rates and photoreactivity change with source and composition (e.g., Stubbins et

464   al. 2011). Because the exact chemical structure of DOM is often unknown, DOM loss (or product

465   formation) is often modeled via the development of "apparent" quantum yields (AQY; Miller et al.

466   2002). The AQY describes the quantitative relationship between DOM breakdown (or photoproduct

467   formation) and the amount of radiation absorbed by DOM (i.e., photoproduct amount per photon light

468   absorbed). The AQY and DOM absorption are defined for individual wavelengths, and the product of

469   AQY, DOM absorption and light availability is integrated across the wavelengths of interest to predict

470   DOM disappearance (or photoproduct formation; e.g., Miller et al. 2002, Swan et al. 2009). Similar to

471   aquatic systems, where the AQY and DOM absorption change with DOM source and composition

472   (Stubbins et al. 2011), predicting photoproduct formation during terrestrial photodegradation may

473   depend on plant litter photoreactivity changes with litter chemistry.

474   While some products of photodegradation are well known (e.g., CO_2, CH_4, CO), not all of the relevant

475   products have been identified. For example, there is little direct evidence of the conversion of litter to

476   SOM by photodegradation (Mayer et al. 2012; Fig. 6), but it has been long hypothesized and was

477   incorporated into Moorhead and Callaghan's (1994) photodegradation model. Even less is known about

478   direct photodegradation of SOM or the contributions of photodegradation to soil N cycling, and no

479   models currently address these processes.

480   As previously noted, solar radiation and photodegradation may interact with biotic decomposition by

481   changing the biodegradability of litter or negatively impacting microbes (Fig. 6). Yet, none of the four

482   terrestrial photodegradation models attempt to account for these interactions, likely because so little is

483   known about them. Failing to account for these interactions will likely result in biased predictions of

484   mass loss in systems exposed to high levels of solar radiation.

485   Developing a global photodegradation model requires understanding how photodegradation interacts

486   with climate. We do not yet have a quantitative understanding of how litter moisture and temperature

487   influence photodegradation rates and photoproduct yields. Results from aquatic systems suggest that

488   photodegradation may be influenced by temperature; Zhang et al. (2006) found that the AQY of CO

489   produced from DOM increased substantially with water temperature (by up to 70% between 0.5 – 32

490   °C). Without understanding of how photodegradation processes change with temperature and moisture,

491   attempts to scale up local photodegradation results to the globe will likely yield inaccurate estimates.

492   In contrast to models of aquatic systems (e.g., Miller et al. 2002), current terrestrial photodegradation

493   models have been inconsistent in parameterizing litter exposure to solar radiation. Thus far, Rozema et

494   al. (1999) took the most thorough approach: mass is lost linearly as a function of radiation exposure

495   while accounting for light extinction through a canopy. Schade and Crutzen's (1999) model predicts

496   global CO evolution from litter as a function of solar radiation, but does not explicitly account for light

497   extinction (an "ecosystem factor" accounts for both light and litter availability). Similarly, Foereid et al.

498   (2011) developed a linear equation that related mass loss to incident radiation, but their model did not

499   account for light extinction. The Moorhead and Callaghan (1994) model did not use solar radiation as a

500   model input. Basing photodegradation or photoproduct yield on the availability of solar radiation is an

501   important first step. It remains to be determined whether it is necessary, as in aquatic models, to

502   account for light extinction, canopy interception, substrate radiation absorption and photoproduct

503   AQYs.

504   Whether terrestrial photodegradation will be best described by simple pool based models (e.g.,

505   Moorhead and Callaghan 1994) and/or linear equations (e.g., Foereid et al. 2011) or by more complex

506   photochemical models (such as those developed for DOM) will only be known when the mechanisms

507   driving terrestrial photodegradation are defined and sufficient data exist to conduct sophisticated model

508   comparisons.

Conclusions

510   Research on the role of photodegradation in the decomposition of terrestrial plant litter over the past

511   decade has fundamentally altered our perception of terrestrial C and N cycling as primarily biotic

512   processes. Current estimates of C fluxes from photodegradation vary widely, but evidence suggests that

513   a substantial fraction of net primary productivity can be returned to the atmosphere via this abiotic

514   process, primarily as CO_2. Research points to photodegradation as a source of other trace gases,

515   including CO, CH_4, ethylene, and trace N gases. Some evidence also suggests that photodegradation may

516   interact with biotic decomposition, potentially increasing microbial respiration rates by producing labile

517   C, but more studies are needed to better understand this interaction (Box 1).

518   Recent work and our meta-analysis show that photodegradation is most important in low latitude

519   ecosystems and ecosystems characterized by low mean annual precipitation. However,

520   photodegradation may also play an important role in climates with highly seasonal rainfall (e.g., Henry

521   et al. 2008) or in mesic environments during very dry years (e.g., Brandt et al. 2010). Still, it is likely that

522   photodegradation plays the largest role in arid and semi-arid ecosystems, where plant litter is highly

523   exposed to solar radiation and where microbial decomposition may be limited by moisture and radiation

524   conditions.

525   Rates of photodegradation are likely influenced by several factors, including temperature, moisture,

526   litter chemistry and level of exposure to solar radiation. While research has revealed much about the

527   climates where photodegradation is important, exactly how photodegradation interacts with changes in

528   temperature and moisture remains unknown (Box 1). Our meta-analysis results indicate that

529   photodegradation increases with litter C/N and area/mass, but the effects of lignin content and litter

530   chemistry in general are unclear. Much of this confusion likely originates from an incomplete

531   understanding of the mechanisms driving terrestrial photodegradation.

532   A critical gap still exists in our understanding of the mechanisms by which photodegradation occurs.

533   Thus far, most terrestrial photodegradation research has failed to differentiate between direct and

534   indirect photochemical mechanisms. Research in aquatic systems and on wood and paper materials

535   suggests that terrestrial ecologists should consider how these distinct mechanisms may differentially

536   affect how litter is photodegraded. Working to better understand the mechanisms driving

537   photodegradation will help us identify the important photo-active plant compounds, photodegradation

538   products, and wavelengths, as well as allow us to improve models of C and N cycling in arid and semi-

539   arid ecosystems.

540   Although many questions about photodegradation in terrestrial ecosystems have yet to be answered

541   (Box 1), results to date indicate that, in arid and semi-arid ecosystems, photodegradation speeds up C

542   (and likely N) losses to the atmosphere and reduces storage in litter and soil organic matter. The results

543   of research on photodegradation patterns and mechanisms will continue to provide critical information

544   for biogeochemical models and advancing understanding of ecosystem and global C and N cycling.

Acknowledgements

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