1 Photodegradation of plant litter in the Sonoran Desert varies by litter type and age

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Abstract

Predicting litter decay rates in arid systems has proved elusive and sunlight (photodegradation) is a potentially important but poorly understood driver of litter decay in these systems. We placed three litter types (*Cynodon dactylon*, *Larrea tridentata* leaves, and *L. tridentata* twigs) in envelopes whose tops either transmitted all solar radiation, filtered UV-B, filtered all UV, or filtered all UV and visible solar radiation, on the soil surface of the Sonoran Desert and assessed mass loss over 14 months. Regardless of treatment, final mass loss was greatest in *C. dactylon* litter and least in *L. tridentata* twig litter, consistent with initial litter characteristics of presumed litter quality; *C. dactylon* had the lowest lignin concentration and lignin:N, and the highest cellulose:lignin and area:mass. Compared to litter in sunlight, excluding solar UV, or UV-B, slowed mass loss of all 3 litter types, and UV-B appeared more effective than UV-A in photodegradation. The relative contribution of UV photodegradation to mass loss increased with litter age. After 14 months, litter exposed to solar UV lost 1.2 (*C. dactylon*), 1.3 (*L. tridentata* leaves) and 1.4 (*L. tridentata* twigs) times as much mass as litter not exposed to UV radiation. The relative contribution of UV photodegradation to mass loss increased with the initial C:N ratio of litter, but was not related to initial lignin concentration or optical properties (i.e. UV and visible absorbance and transmittance) of litter. Within all litter type by treatment combinations, there was a strong positive correlation between litter mass loss and ash concentration. In some cases, a discontinuity in this relationship was detected, suggesting a threshold ash concentration, above which further mass loss was negligible. We expected these thresholds to be most prevalent in sunlight, because soil films could prevent sunlight from reaching litter and thereby minimize photodegradation. Contrary to expectations, thresholds were more common in shade or UV filter treatments, suggesting that reductions in photodegradation attributable to soil films were not typically responsible. The effect of shading, which likely enhanced microbial degradation via higher relative humidity due to lower temperatures, depended on litter type and time. Compared to litter in sunlight, mass loss of shaded litter was greater over the initial 3

months in all litter types, illustrating that microbial degradation in shade was greater than photodegradation in sunlight. These differences in mass loss between shaded and sunlit litter increased over the 14 month experiment in *L. tridentata* twigs, declined in *L. tridentata* leaves, and disappeared within 6 months in *C. dactylon*, illustrating that the timing of this shift in the dominance of photodegradation versus microbial degradation was highly dependent on litter type. In a second experiment, we reduced microclimate differences among sun and shade treatments, pre-sterilized litter to reduce microbial degradation, and examined the mass loss of young and old and *L. tridentata* leaf litter after 53 days outdoors. Consistent with our first experiment, mass loss attributable to photodegradation was greater in old than young litter. Unsterilized litter exposed to sunlight (UV and visible) lost 1.3 (young) and 1.5 (old) times as much mass as shaded litter. Pre-sterilized litter exposed to sunlight lost 11.4 (young litter) and 45.9 (old litter) times as much mass as shaded litter. These large differences in pre-sterilized litter were the result of the very small mass loss of shaded litter ($\leq 0.2\%$), together with modest losses of sunlit litter ($< 5\%$). Taken together, our findings suggest that as litter aged, microbial degradation became a weaker driver of mass loss, while photodegradation became stronger.

Keywords: *Cynodon dactylon*; *Larrea tridentata*; Litter decomposition; Photodegradation; Soil-litter mixing; UV radiation

1. Introduction

Plant litter decomposition is a key pathway in the C cycle and releases more C annually than fossil fuel combustion (Gholz et al., 2000). Climatic factors, particularly moisture availability and temperature (Meentemeyer, 1978; Gholz et al., 2000), along with initial litter chemistry (e.g. C:N, lignin:N; Melillo et al., 1982; Hobbie, 1992), have been used to develop empirical relationships that can predict litter decay rates in many terrestrial ecosystems (Meentemeyer, 1978; Swift et al., 1979; Aber and Melillo, 1982). However, these relationships do not accurately

predict litter decay rates in many semi-arid and arid ecosystems (Whitford et al., 1981; Schaefer et al., 1985; Whitford, 2002; Kemp et al., 2003; Austin and Vivanco, 2006; Parton et al., 2007; Adair et al., 2008; Vanderbilt et al., 2008). For example, Parton et al. (2007) and Adair et al. (2008), using a 10-yr data set from 7 biomes, found that litter mass loss was well predicted by the climatic decomposition index, which incorporates temperature and moisture, with the notable exception of arid sites, where decay rates were greater than expected. Both groups suggested that photodegradation by solar UV radiation (UV; 280-400 nm) may be responsible.

Research over the past 10 years has documented that exposure to solar radiation can drive litter mass loss, although its significance is not well understood. In some cases, solar UV can be a dominant driver of litter mass loss, exceeding the magnitude of biotic drivers (Austin and Vivanco, 2006; Rutledge et al., 2010), while in other cases solar UV appears to have little effect on litter mass loss (Brandt et al., 2007; Uselman et al., 2011). In a recent meta-analysis of litter photodegradation studies, King et al. (2012) found that removing all solar radiation (UV and visible), or UV, reduced litter mass loss an average of 45 and 25%, respectively, suggesting that photodegradation often has a substantial influence on litter decomposition and nutrient cycling, particularly in arid systems where solar irradiance is high and biotic drivers may be constrained by water limitations.

Several wavebands of solar radiation can drive litter mass loss, including UV-B radiation (UV-B, 280-320 nm; Austin and Vivanco, 2006; Brandt et al., 2007; Day et al., 2007; Smith et al., 2010), UV-A radiation (UV-A, 320-400 nm; Brandt et al., 2009), and lower wavelengths of visible radiation (i.e. 400-550 nm; Austin and Vivanco, 2006; Brandt et al., 2009; Austin and Ballaré, 2010). Lignin, a group of aromatic polymers covalently bound to other cell wall constituents, is one putative target of solar degradation in litter. Exposure to sunlight (Henry et al., 2008), and specifically UV-B (Rozema et al., 1997; Day et al., 2007), and to a lesser extent UV-A and low-wavelength visible (Austin and Ballaré, 2010), accelerates lignin loss from litter, consistent with lignin's general absorption spectrum (Austin and Ballaré, 2010). However, King

et al. (2012) found that the relative contribution of UV photodegradation to mass loss was not correlated with the initial lignin concentration of litter, suggesting that high lignin concentrations do not predispose litter to greater photodegradation. In some cases, photodegradation is accompanied by losses of other compounds (Brandt et al., 2007; Day et al., 2007; Gallo et al., 2009; Lin and King, 2014) and neither the chemical targets, nor the photochemical mechanisms, which may be direct or indirect, are well understood (King et al., 2012).

The optical properties of litter have not received much attention in the context of photodegradation, but differences among litter may predispose some types to greater photodegradation. For example, litter that absorbs more sunlight might be more prone to photodegradation. Alternately, litter that transmits more solar radiation might be more prone to photodegradation since higher transmittance could indicate higher fluxes of radiation inside litter, where targets may be more abundant.

Another factor that has recently been recognized to have a potentially important role in litter decomposition in arid systems is soil-litter mixing (Throop and Archer, 2007; Barnes et al., 2015). Soil particles, microbes and microbial exudates, often accumulate and form a “soil film” that adheres to litter surfaces, and this can be particularly pronounced in arid systems. Litter ash concentration, which may provide an index of soil accumulation on litter, has been found to be positively correlated with litter mass loss (Throop and Archer, 2007, 2009; Brandt et al., 2010; Hewins et al., 2013), suggesting that soil films accelerate litter decay. Explanations for this include that soil deposition abrades litter surfaces which could facilitate leaching or microbial colonization, that soil is a vector for microbes, or that soil buffers temperature and moisture regimes in litter which could enhance microbial activity (Throop and Archer, 2007, 2009; Lee et al., 2014). On the other hand, soil films could also slow litter decay, via filtering sunlight before it reaches the litter surface and thus reducing photodegradation (Barnes et al., 2012).

In this study we examined how exposure to different wavebands of solar radiation influenced decomposition of litter placed on the soil surface of the Sonoran Desert for 14

months. Litter was placed in envelopes whose tops absorbed different wavebands to compare the effectiveness of UV-B, UV-A and visible radiation on mass loss. We assessed three types of litter which had contrasting initial chemistry and optical properties (i.e. UV and visible absorbance and transmittance). Along with mass loss, we determined how our treatments influenced litter chemistry to provide clues as to what compounds might be involved. We also examined the relationship between mass loss and litter ash concentrations to assess whether soil films appeared to accelerate decay, and whether there was any indication this slowed photodegradation. Results from this experiment suggested that the relative contribution of photodegradation to mass loss increased with litter age. Additionally, it appeared that our solar exclusion treatments, particularly our shade treatment, not only prevented photodegradation, but probably accelerated microbial-driven mass loss, thereby confounding our assessment of the relative contribution of photodegradation to litter mass loss. In view of this, in a second experiment we reduced microclimate differences between sunlight and shade treatments, and employed a sterilization treatment and protocols that reduced microbial degradation. In this second experiment we assessed how exposure to sunlight for 53 days influenced the mass loss of young and old litter.

2. Materials and methods

2.1. Experiment 1

2.1.1. Study site and litter collection

Experiment 1 was conducted in the lower Sonoran Desert in a conservation area at the Desert Botanical Garden, Phoenix, AZ, USA (33.5°N, 111.8°W). Mean annual air temperature is 22.5°C and total annual precipitation averages 195 mm. Clear, dry skies are prevalent for much of the year, with Phoenix receiving an average of 85% of annual possible sunshine (Cervany, 1996), and along with its low latitude, results in relatively high UV irradiance. Although we did not monitor UV irradiance during our experiments, subsequent monitoring at our site has confirmed relatively high UV doses. For example, daily biologically effective UV-B doses

(weighted with the generalized plant action spectrum (Caldwell, 1971) normalized to 300 nm) average 1.2 and 4.9 kJ·m⁻² over 2-month periods centered on the winter and summer solstices, respectively (Day, unpublished data).

The plant community was composed of widely-spaced *Larrea tridentata* (DC.) Coville (creosote bush) shrubs. The study plot was in an unshaded area, void of shrubs, on a level, alluvial terrace. We collected senescing terminal branches (containing attached yellow leaves) of *L. tridentata* growing adjacent to our study plot in June-August 2007. Leaves and small diameter (≤ 3 mm) terminal shoots were separated and are referred to as *L. tridentata* leaf or twig litter, respectively. Litter of *Cynodon dactylon* (L.) Pers. (bermudagrass) was collected over the same period from recently senesced plants in an adjacent wash. Recently senesced plants were cut ≈ 2 cm above the soil surface. Any panicles, along with leaves or culms that did not appear to have recently senesced (i.e. older material) were removed, and the remaining material was cut into pieces ≈ 6 cm long. This grass litter was a mixture of $\approx 90\%$ leaves and $\approx 10\%$ culms (dry-mass basis). We chose these litter types in part because they represented contrasts in initial litter chemistry (see Results).

2.1.2. Treatments

Litter was air dried in the laboratory for at least 30 d, and placed in envelopes (10x10 cm) whose tops were constructed of different filter materials that transmitted different solar wavebands, representing radiation treatments: (1) A “sunlight” treatment that transmitted $>80\%$ of solar UV and visible radiation (filter: Aclar Type 22A film, Proplastics, Linden, NJ, USA). (2) A “no UV-B” treatment that did not transmit most UV-B radiation (filter: Mylar-type Cadco clear polyester film, Cadillac Plastic & Chemical, Phoenix, AZ, USA). (3) A “no UV” treatment that did not transmit most solar UV radiation (filter: Courtgard film, CPFilms, Martinsville, VA, USA). (4) A “shade” treatment that did not transmit UV or visible radiation (filter: Mylar film sprayed with flat white paint (general purpose flat white, Rust-oleum, Vernon Hills, IL, USA). All filters were

0.13 mm thick. We drilled 81 holes (1-mm dia, placed at 1 cm² centers) in each filter top to allow air and precipitation to enter envelopes.

We used a custom integrating sphere system (Supplementary Information 1) to measure the UV and visible transmittance (*t*) spectra of the filter tops (Supplementary Information 2a). Spectra were measured in 1-nm increments from 280-700 nm.

The bottom of envelopes was 153-μm mesh screen (Nitex bolting cloth, Wildlife Supply, Buffalo, NY, USA), which allowed air, water and microbial movement into envelopes. Envelope edges were sealed with UV/visible-transparent tape. At each envelope corner we attached a 2-cm long tab, through which we placed a galvanized steel nail to anchor envelopes firmly to the soil surface.

Envelopes received either 2 (+/- 0.05) g (air dried) of *C. dactylon*, 6 (+/- 0.04) g of *L. tridentata* leaf or 4 (+/- 0.04) g of *L. tridentata* twig litter. Different amounts of each litter type were used, based in part on the availability of litter. Litter envelopes were placed on the soil surface of the plot on 14 December 2007, coinciding with the period when litterfall in *C. dactylon* and *L. tridentata* is probably most common (Chew and Chew, 1965). We used a completely random design with envelopes randomly assigned to locations within a grid in the plot. The experiment comprised 3 litter types x 4 radiation treatments x 4 collection times x 10 replicate envelopes for a total of 480 envelopes. Ten replicate envelopes of each litter type/treatment combination were collected on 17 March, 14 June, and 18 October 2008, and 14 February 2009 after approximately 3, 6, 10 and 14 months in the field. We noticed that the tape seals on some envelopes were beginning to fail in July 2008, at which time all envelopes were replaced. Monthly measurements of filter top transmittance (made on extra envelopes) confirmed that transmittance did not change over the experiment. During weekly inspections, any dust observed on envelope tops was removed by gentle brushing.

2.1.3. Weather and microclimate

To assess whether precipitation and temperature regimes during our experiment were typical, we used weather data from Sky Harbor International Airport (6 km from our site) to compare conditions during our experiment to the historical average (previous 20 yr). We assessed litter microclimate by measuring air temperature and relative humidity in extra envelopes of each treatment (containing *L. tridentata* leaf litter) from January through June 2008. Air temperatures were measured with fine-wire (0.5 mm dia) thermocouples placed below litter of 5 envelopes of each filter type. Relative humidity in each filter type was measured with a humidity probe (HMP35C, Vaisala, Woburn, MA, USA) that was placed below litter in one extra envelope of each filter type. Visible irradiance (PAR) was measured with a quantum sensor (LI-190SA, Li-COR, Lincoln, NE, USA) in the center of the plot. Sensor signals were collected every minute and summarized as hourly means with dataloggers (CR23X, Campbell Scientific, Logan, UT, USA).

2.1.4. Litter mass loss and litter characteristics

Ten subsamples of each initial litter type were oven dried (60°C for 48 h) and ashed (550°C for 6 h in a muffle furnace), to determine initial oven-dry, ash-free mass. We also measured the one-sided silhouette surface area (i.e. the projected or sunlit area) of 10 intact pieces of each litter type on a scanner and determined their oven-dry mass, to assess area:mass. Following collection of litter envelopes from our plot, contents were gently poured onto white paper, and extraneous material was removed. The remaining litter sample contained litter along with any soil film that adhered to its surface. The sample was oven dried, a subsample was ashed, and mass loss was calculated on an oven-dry, ash-free basis.

We analyzed the chemistry of 10 initial subsamples of each litter type, and litter collected from each envelope at the end of the experiment. Subsamples were ground (1 mm) in a Willey Mill, dried at 60°C and analyzed for cellulose and lignin with sequential digestion generally following Van Soest (1967) using a fiber analyzer (ANKOM, Macedon, NY, USA). Subsamples were digested in acid detergent fiber solution to estimate the cellulose plus lignin fraction,

agitated in 72% H₂SO₄ for 3 h, and ashed to estimate cellulose and lignin concentrations. We did not digest in a neutral detergent solution or estimate hemicellulose concentrations. Another set of initial and final subsamples were finely ground in a ball mill and C and N concentrations were assessed with a flash combustion elemental analyzer (PE2400, PerkinElmer, Waltham, MA, USA).

The UV and visible transmittance and reflectance (*r*) spectra of 4 pieces of each initial litter type were measured with the integrating-sphere system (Supplementary Information 1). For *C. dactylon* and *L. tridentata* leaf litter, measurements were made on adaxial and abaxial surfaces. Differences between surfaces were negligible, and the mean was used as a replicate. Absorbance (α) was calculated as $\alpha = 100 - t - r$. Because photodegradation appears driven by UV and lower wavelength visible (<550 nm) we summarized results by comparing mean *t* and α in 50-nm increments from 300-500 nm.

2.2. Experiment 2

2.2.1. Rationale

In Experiment 1 we were unable to fully assess photodegradation by full sunlight (visible and UV) because microbial degradation in the shade treatment appeared to be substantially greater than in other treatments. This appeared primarily due to lower temperature in the shade, which led to higher relative humidity. In view of this, in Experiment 2 we employed sun and shade treatments designed to reduce temperature differences between these treatments. Along with reducing microclimate differences between treatments, we also attempted to reduce microbial activity in all treatments. We accomplished this in several ways: litter was not in close proximity to soil, contamination by dust or air-borne microbes was reduced by minimizing holes in envelope tops and sealing bottoms with film (rather than mesh), and litter was brought indoors during rainfall events to prevent contact with liquid water. Additionally, we also included a sterilization treatment to reduce microbial abundance. Our findings from Experiment 1 also

suggested that UV photodegradation increased as litter aged. In view of this, we also incorporated a litter age (young versus old) treatment.

2.2.2. Litter collection and preparation

Leaf litter of *L. tridentata* was collected from the ground surface under the canopy of *L. tridentata* shrubs adjacent to our plot in Experiment 1. This litter was sorted as to age class based upon its color. Our past (Day et al., 2007) and subsequent experiments with *L. tridentata* leaf litter found that young litter has a beige or light brown color that persists for up to 3 months under field conditions at our site. After 6 months this litter attains a dark brown color, which we refer to as old litter. Very old litter attains a gray color, partly because of a soil film that develops on its surface. For this experiment we used young litter and old litter. Litter of intermediate color or very old (gray) litter was not used. Hence, we do not know the exact age of the litter we used in this experiment, but are confident that it was relatively young ($\approx \leq 3$ months) or old ($\approx \geq 6$ months). Only whole (intact) pieces of leaf litter were used. Following sorting, litter was air dried in the laboratory for 1 month.

2.2.3. Treatments

Litter envelopes (8 x 8 cm) were constructed of unpainted Aclar ("sun") or painted Aclar tops that were opaque ("shade"). To reduce temperature differences of litter between sun and shade treatments, we chose to paint the tops of shade envelopes such that they mimicked the solar absorbance of the litter they contained. Our rationale was that a main factor controlling litter temperature under a transparent envelope top would be the amount of solar radiation absorbed by the litter, while the main factor controlling temperature under an opaque (shade) top would be the amount of radiation absorbed by top. Hence, if we matched the solar absorbance of an opaque top to that of its litter, we could reduce temperature differences between sun and shade treatments within a litter type. Because the solar absorbance and color of young and old litter differed, we used different colors for their shade tops. Tops of young-litter envelopes were painted with a flat light brown spray paint (satin nutmeg enamel, Rust-oleum),

while tops of old-litter envelopes were painted with a darker flat brown paint (flat brown enamel, Rust-oleum). The UV-visible absorbance of these colored tops was similar to their respective litter; mean UV-visible absorbance of light-brown tops ($83.0 \pm 0.4\%$ SE) was very similar to young litter ($84.1 \pm 0.6\%$), and that of dark-brown tops ($91.9 \pm 0.1\%$) was very similar to old litter ($92.2 \pm 0.2\%$) (Supplementary Information 2b).

To reduce potential contamination by microbes, envelopes had Aclar bottoms. Each envelope top had one hole (1-mm dia) in each upper corner to allow air exchange. The sterilization treatment entailed placing air-dry litter in an oven at 121°C for 20 minutes. We acknowledge that this sterilization treatment likely altered the chemistry and quality of litter. However, other approaches that have been used to minimize microbial activity in outdoor litter experiments involve potentially unwanted effects that could also confound results (King et al., 2012). We placed 0.40 g (± 0.04 g) of air-dry litter in each envelope. Initial subsamples ($n=8$) of each litter type were oven dried and ashed to allow initial mass to be expressed on an oven-dry, ash-free basis.

The experiment involved 2 radiation treatments (sun or shade), 2 litter age classes (young or old), 2 sterilization treatments (sterilized or unsterilized), and 8 replicate envelopes of each combination for a total of 64 envelopes. One litter envelope of each treatment combination was randomly assigned to a location on one of eight flat, white plastic trays that served as experimental blocks. Envelopes were held in place by double-sided tape between the envelope bottom and the tray. Trays were placed adjacent to each other in an unshaded area on the roof of the Life Science E-wing building at Arizona State University, Tempe, AZ, on 24 March 2011. The location of trays was rotated weekly. Because of impending precipitation, trays were brought indoors and placed in a dark room (20°C , relative humidity 20-25%) on 3 days (6, 9 and 10 April 2011), providing a total of 53 days of outdoor exposure. Envelopes and litter were not exposed to liquid water (precipitation or dew) during the experiment. At the end of the

experiment, on 18 May 2011, litter was oven-dried and ashed, and mass loss was expressed on an oven-dry ash-free basis. We did not assess chemistry of final litter.

We tested the effectiveness of our sterilization treatment by assessing microbial abundance in a parallel experiment. Extra litter was placed in shade envelopes on plastic trays on the rooftop. This test involved 2 sterilization treatments (sterilized or unsterilized), 2 litter age classes (young or old) and 5 replicate envelopes of each treatment combination. Fungal and bacterial colonization was assessed at the end of experiment by extracting 100 mg of ground, mixed litter in 100 ml of sterile water and plating on agar containing either a fungicide (natamycin) or a bactericide (novobiocin) generally following Brandt et al. (2009). After incubating at 25°C for 2 d, we counted colony-forming units (CFUs). Numbers of fungal and bacterial CFUs from sterilized litter were significantly lower than unsterilized litter ($P < 0.0001$; Supplementary Information 3). Numbers of CFUs did not differ between young and old litter ($P > 0.09$). While the CFU approach is biased in that it ignores some microbes, the dramatically lower numbers of CFUs we found in sterilized litter illustrates that microbes were likely less abundant.

We used 2 additional trays containing litter samples to assess litter temperatures in treatments and in adjacent free litter. Fine-wire thermocouples were attached to the lower surface of litter in 3 sun and shade envelopes of each litter type. Additionally, thermocouples were attached to free litter placed on the surface of trays and held in place with double-sided tape, to assess temperatures of free litter. Relative humidity and PAR were measured at litter height in the center of one tray. Signals from sensors were collected every minute and summarized as hourly means.

2.3. Data and Statistical analyses

In Experiment 1, a 3-way ANOVA was used to assess time, litter type and treatment effects on mass loss using JMP (SAS Institute, Cary, NC, USA). All data sets gave Wilk-Shapiro/Rankit test values > 0.96 and no data were transformed. Differences among types in

initial litter parameters, and between initial and final parameters within a type, were assessed with Tukey's HSD test. We calculated decay constants (k) with a single exponential model, $X_t/X_o = e^{-kt}$, where X_o and X_t are the initial ash-free dry mass and the mass at time t , respectively. Curve-fitting of the negative exponential curves, rather than linear regressions on log-transformed data (Adair et al., 2010), were done using all data ($n=50$ for each litter type/treatment combination) with Sigmaplot (Systat Software, San Jose, CA, USA).

To quantify photodegradation in Experiment 1, we calculated the response ratio (RR) as the ratio of mass loss of litter in full sunlight to that of litter not exposed to UV (RR_{uv}) or not exposed to UV-B (RR_{uv-b}). The greater the RR value above 1.0, the more mass loss attributable to UV (or UV-B) exposure. For example, an RR_{uv} value of 1.5 indicates that litter exposed to UV lost 1.5 times as much mass as litter not exposed to UV. In Experiment 2, we used the same approach, in this case calculating RR_{sun} as the ratio of mass loss in sunlight to that in shade.

In some cases, the relationship between litter dry mass and ash concentration suggested a discontinuity or threshold ash concentration, above which mass loss was negligible. To test for discontinuity, we used a piecewise linear regression model (SegReg software (<http://www.waterlog.info/segreg.htm>)) to detect and identify breakpoints following Guénon et al. (2011). If the piecewise model was significant, and had a greater coefficient of determination than the simple linear model, it was deemed a better fit.

We summarized air temperature and relative humidity in Experiment 1 by calculating monthly averages over diel, diurnal and nocturnal hours. We separated diurnal from nocturnal periods by defining the former as those hours when maximum hourly PAR $>2 \mu\text{mol m}^{-2} \text{s}^{-1}$. We used the mean of each temperature sensor over a time period as a replicate, and Tukey's HSD test to assess differences among treatments. The same approach was used with the litter temperature data in Experiment 2, using averages over the 53 days that the experiment was outdoors.

In Experiment 2, a 3-way ANOVA was used to assess sunlight, litter age and sterilization effects on litter mass loss. We used Tukey's HSD test to assess differences in CFUs and in initial chemistry among litter types. Data sets gave Wilk-Shapiro/Rankit test values >0.97 and no data were transformed

3. Results

3.1. Experiment 1

3.1.1. Litter mass loss

Litter type, radiation treatment and time had significant effects on litter mass loss and all interactions were significant (Table 1). Concerning litter type, after 14 months, *C. dactylon* litter lost the most mass while *L. tridentata* twig litter lost the least mass within a given treatment (Fig. 1). For example, *C. dactylon* litter in full sunlight lost 59% of its mass, compared to 33% for *L. tridentata* leaf litter and 19% for twigs. As such, decay constants within a given treatment were highest for *C. dactylon*, intermediate for *L. tridentata* leaves and lowest for twigs (Table 2).

Filtering UV-B, or all UV, slowed mass loss of *C. dactylon* litter. After 14 months, *C. dactylon* litter in full sunlight lost 59% of its mass, but when UV-B was filtered it lost only 52%, and when all UV was filtered it lost only 49% of its mass (Fig. 1a). In *L. tridentata* leaf and twig litter, filtering UV-B or all UV radiation also slowed mass loss compared to litter in sunlight; leaf litter in sunlight lost 33% of its mass, compared to 27 and 23% for litter not exposed to UV-B or UV, respectively (Fig. 1b). Twig litter in sunlight lost 19% of its mass, compared to 16 and 14% for litter not exposed to UV-B or UV, respectively (Fig. 1c).

RR_{UV} was lowest for *C. dactylon* and greatest for *L. tridentata* leaves (Fig. 2a), illustrating that the relative contribution of UV photodegradation to mass loss was lowest in *C. dactylon* and greatest in *L. tridentata* leaf litter. For example, at the end of the experiment, litter exposed to UV lost 1.2 (*C. dactylon*), 1.3 (*L. tridentata* leaves) and 1.4 (*L. tridentata* twigs) times as much mass as litter not exposed to UV. Within a litter type, RR_{UV} generally increased with time,

illustrating that UV photodegradation increased with litter age. As expected, RR_{uv-b} values were lower than RR_{uv} , but generally showed similar trends in terms of litter type and age (Fig. 2b).

The influence of shading on mass loss strongly depended on litter type and time. Compared to litter in sunlight, shaded litter initially lost more mass in *C. dactylon*, but this effect disappeared by 6 months and by the end of the experiment shaded litter had lost the least mass (Fig. 1a). *L. tridentata* leaf and twig litter in shade also lost more mass than litter in sunlight, but in contrast to *C. dactylon*, this effect persisted throughout the experiment (Fig. 1 b,c). In the case of *L. tridentata* leaf litter, differences in mass loss between shade and sun generally declined through time, while differences in twig litter increased over the experiment.

3.1.2. Litter microclimate and weather

Air temperatures in litter envelopes were generally similar among the sunlight, no UV-B and no UV treatments; when averaged across the whole monitoring period, the mean diel, diurnal and nocturnal temperatures of these 3 treatments were within 0.3°C of each other. Nonetheless, monthly average temperatures in the no UV-B and no UV treatments were lower than in sunlight in June (all periods) and February and May (diurnal periods) (Fig. 3). The largest differences occurred among these treatments during diurnal periods in June, when temperatures averaged 54.7(sunlight), 52.7 (no UV-B) and 51.7°C (no UV) (Fig. 3b). Relative humidity was generally similar among these 3 treatments (Fig. 3d-f).

The shade treatment was cooler and more humid than the other treatments (Fig. 3). Averaged across the whole monitoring period, temperatures averaged 1.4, 3.5 and 0.5°C lower in the shade than in sunlight over diel, diurnal and nocturnal periods, respectively. The largest differences occurred during diurnal periods in June when temperatures averaged 45.3 in the shade compared to 54.7°C in sunlight (Fig. 3b). Relative humidity was consistently higher in the shade, and these differences were greatest during diurnal periods of cooler months (Fig. 3d-f). Averaged across the whole monitoring period, relative humidity in the shade averaged 4.5, 6.3 and 3.1% higher than in sun over diel, diurnal and nocturnal periods, respectively. Higher

relative humidity in shade was the result of lower temperature (and saturation vapor pressure), rather than air vapor pressure, which was similar among treatments (not shown).

Precipitation and temperature regimes during the experiment were generally typical of historical averages (Supplementary Information 4). Total precipitation was 245 mm, slightly higher than the historical average (225 mm) due mainly to a wetter mid-June to mid-October period. Air temperatures during the experiment averaged 22.7°C compared to a historical average of 22.2°C.

3.1.3. Litter characteristics

Litter types differed in initial chemistry and presumed substrate quality, with *C. dactylon* being of highest quality and *L. tridentata* twigs lowest (Table 3). *Cynodon dactylon* had the lowest lignin concentration, lignin:N and C:N ratio, and the highest cellulose:lignin ratio. *Larrea tridentata* twigs had the highest lignin concentration and lignin:N, and the lowest cellulose:lignin ratio. Litter area:mass was highest in *C. dactylon* and lowest in *L. tridentata* twigs (Table 3).

In *C. dactylon* litter, final concentrations of C and N, and C:N ratios were lower than initial values (Fig. 4). In *L. tridentata* leaf litter, final concentrations of N were higher than initial values, and final C:N ratios were lower. Shaded leaf litter had the highest N concentrations and lowest C:N ratio. In twig litter, differences between initial and final chemistry were modest.

Exposure to sunlight facilitated the loss of lignin from *C. dactylon* and *L. tridentata* leaf litter and losses generally increased with exposure to more solar wavebands (Fig. 5a,b). *Cynodon dactylon* litter lost large amounts of cellulose in all treatments, with losses increasing with exposure to more solar wavebands. *Larrea tridentata* leaf litter also lost cellulose, but only in the shade. No losses of lignin or cellulose were detected in twig litter (Fig. 5c).

The UV optics were similar among initial litter types, with all having high absorbance (>94%) and low transmittance (<1%; Table 4). Visible (400-500 nm) optics differed among litter types, with *C. dactylon* having lower absorbance and higher transmittance than both *L. tridentata* litters.

3.1.3. Litter decay and ash concentration

Litter mass remaining was strongly correlated with ash concentration in all litter type/treatment combinations ($P < 0.0001$) and coefficients of determination of linear regressions were relatively high ($r^2 = 0.37-0.92$; Fig. 6). In some cases, the pattern of these relationships suggested a threshold ash concentration, above which further mass loss was negligible. Piecewise linear regression analysis identified threshold ash concentrations, above which mass losses appeared negligible, in five litter type/treatment combinations. In *C. dactylon* litter, thresholds occurred at 33.2% ash in no UV, and 30.7% ash in shade (Fig. 6c,d). In *L. tridentata* leaf litter, thresholds occurred at 13.2% ash in sunlight, 15.2% in no UV, and 18.5% in shade (Fig. 6e,g,h).

3.2. Experiment 2

3.2.1. Litter microclimate

Differences in litter temperatures in Experiment 2 between sunlight and shade treatments within a litter type were modest, and were not significantly different (Table 5); the highest differences occurred during diurnal periods when sunlit litter averaged 1.2 (young litter) and 1.6°C (old) higher than shaded litter. Differences in temperature between young and old litter within a given treatment were also modest, and were not significant ($P > 0.05$, Tukey's HSD test). The temperature of sunlit litter was significantly higher than free litter during all periods. Relative humidity at litter height averaged 28% (not shown). Over the experiment, hourly relative humidity at litter height averaged $\geq 50\%$ for 185 hrs (14.5% of the time), $\geq 60\%$ for 92 hr (7.2%), and 70-76% for 16 hours (1.3%).

Compared to Experiment 1, our experimental approach in Experiment 2 did reduce differences in temperature between sunlight and shade treatments. We assessed this by calculating the average differences in temperature between these treatments over the same days of the year (24 March - 18 May) in each experiment. In Experiment 1, temperatures in sunlight averaged 2.4 (diel), 4.3 (diurnal) and 0.6°C (nocturnal) higher than in shade. In contrast,

in Experiment 2, temperatures of young litter in sunlight averaged 0.8 (diel), 1.6 (diurnal) and -0.1°C (nocturnal) higher than in shade; temperatures of old litter in the sunlight averaged 0.8 (diel), 1.2 (diurnal) and -0.2°C (nocturnal) higher than in shade. These differences between sunlight and shade of both young and old litter in Experiment 2 were significantly lower than differences in Experiment 1 ($P < 0.05$, Tukey's HSD).

3.2.2. Litter chemistry

Old *L. tridentata* leaf litter at the beginning of Experiment 2 had a slightly lower C concentration and C:N ratio, and higher N and ash concentrations, than young litter (Supplementary Information 5). These differences between young and old litter are consistent with the changes we observed in *L. tridentata* leaf litter over Experiment 1 (Fig. 4).

3.2.3. Litter mass loss

Sunlight, litter age and sterilization had significant effects on litter mass loss, and sunlight x litter age and sunlight x sterilization interactions were significant (Fig. 7). Specifically, litter in sun lost more mass (5.5%) than shaded litter (2.7%), old litter lost more mass (4.5%) than young litter (3.5%), and unsterilized litter lost more mass (6.2%) than sterilized litter (1.7%; Fig. 7b). Consistent with our predictions, sunlight had a greater effect on mass loss of old than young litter, and on sterilized than unsterilized litter (Fig. 7c). RR_{sun} , the ratio of mass loss under sunlight to mass loss under shade, was greater in old litter and this was particularly notable in sterilized litter. Specifically, RR_{sun} of sterilized litter was 45.9 for old litter versus 11.4 for young litter (Fig. 7a). In contrast, RR_{sun} of unsterilized litter was 1.5 for old litter versus 1.3 for young litter. It should be noted that the high RR_{sun} values of sterilized litter (45.9 and 11.4) result from the very small mass loss of shaded litter ($\leq 0.2\%$). The mass loss of sunlit litter was relatively modest ($< 5\%$), but when divided by the small losses in the shade, results in large RR values. Litter mass remaining was not correlated with ash concentration in any litter type/treatment combination ($P > 0.10$; not shown). Microbial degradation in sterilized treatments appeared

minimal since sterilized litter in the shade (where photodegradation was absent), retained 99.8% (young litter) and 99.9% (old) of its initial mass (Fig. 7a).

4. Discussion

4.1. General decomposition rates and relationship to litter characteristics

The decomposition rates we found in Experiment 1 are similar to those reported from other arid systems. For example, *L. tridentata* leaf litter under shrub canopies in the Chihuahuan Desert of New Mexico lost 42% mass after 14 months (Kemp et al., 2003) and had annual loss rates of 35% (Schaefer et al., 1985) and 43% (Strojan et al., 1987). We found shaded *L. tridentata* leaf litter lost 39% mass after 14 months (Fig. 1b), and had an annual loss rate of 36%. The decay constants we found for leaf litter ranged from 0.23-0.74 yr⁻¹ (Table 2), which are similar to those reported by Throop and Archer (2007) for leaf litter in the Sonoran Desert (0.28-0.73 yr⁻¹).

The differences in decomposition rates among litter types we found in Experiment 1 are consistent with expectations based upon initial litter chemistry and presumed substrate quality for microbes. For example, decomposition of *C. dactylon* was fastest within a given treatment (Fig. 1, Table 2), and this litter had the lowest initial lignin concentration, C:N and lignin:N ratios, and the highest N concentration and cellulose:lignin ratio (Table 3). Decomposition was slowest in *L. tridentata* twigs and this litter had the highest lignin concentration and lignin:N ratio, and the lowest cellulose:lignin ratio. The faster decay of *L. tridentata* leaves versus twigs is consistent with a previous study at the same site (Day et al., 2007). While abiotic processes such as photodegradation can be significant drivers of decomposition in arid systems, our findings are consistent with Throop and Archer (2009), who reviewed decomposition in drylands and concluded that differences in decay rates among litter types generally follow expectations based on traditional chemical indices of substrate quality for microbial degradation.

Area per mass of initial litter was highest in *C. dactylon* and lowest in *L. tridentata* twigs (Table 3), and hence, positively related to decay rates, a generalization that holds true across

diverse sets of litter types (Aerts, 1995; Cornelissen, 1996; Cornelissen et al., 1999; Pietsch et al., 2014). Low area:mass is a consequence of thicker or denser litter pieces, and is positively correlated with leaf longevity, thicker walls (Reich et al., 1997), more sclerified or lignified tissue (Castro-Díez et al., 2000), higher tensile strength and secondary metabolite concentrations, as well as lower N concentrations (Pietsch et al., 2014), all of which would likely make litter less amenable to microbial degradation.

4.2. Magnitude of photodegradation and relationship to litter characteristics

Compared to litter in full sunlight, excluding UV radiation slowed the decay of all litter types over Experiment 1 (Fig. 1), illustrating that UV photodegradation was a significant driver of mass loss. By the end of the experiment, litter exposed to UV radiation lost 1.2 (*C. dactylon*), 1.3 (*L. tridentata* leaves) and 1.4 (*L. tridentata* twigs) times as much mass as litter not exposed to UV (Fig. 2). The magnitude of UV photodegradation was well within the range found in other field studies that have excluded solar UV radiation. For example, in their meta-analysis, King et al. (2012) found that the average RR_{UV} for litter mass loss in solar UV exclusion studies was 1.3.

Our experimental approach differed from most field photodegradation assessments in that we used filter envelopes, rather than litterbags (i.e. meshbags), to constrain litter. It is likely that our envelope approach elevated litter temperatures (relative to free litter) more so than litterbags. Should higher temperatures promote photodegradation or thermal emission (Lee et al., 2012) or reduce microbial degradation, assumed photodegradation losses may have been greater with our approach compared to free litter. However, we based our assessments of photodegradation on comparisons of sunlight and no UV treatments in Experiment 1, and on sunlight and shade treatments in Experiment 2, and the differences in temperature between these treatments were relatively modest (Fig. 3, Table 5). Hence, we suspect that elevated temperatures did not introduce a large bias in our estimates of the magnitude of photodegradation. Consistent with this, the RR_{UV} values we found in Experiment 1 ranged from 1.2 - 1.4, being well within the range reported by King et al. (2012) in their meta-analysis, and

very close to the average RR_{UV} that they reported for all solar UV exclusion studies (i.e. 1.3). Our envelope approach also likely reduced the amount of precipitation reaching litter, as well as the extent of soil deposition on litter, more so than litterbags. As such, we could expect that leaching or microbial-driven losses might be lower from litter in our envelopes. However, we would expect these effects to be similar among treatments in Experiment 1, such that our approach would provide valid estimates of the magnitude of UV photodegradation. Furthermore, the mass loss rates we observed for shaded *L. tridentata* leaf litter are very similar to those reported from studies in the Southwestern USA that employed litterbags (Schaefer et al., 1985; Strojan et al., 1987; Kemp et al., 2003).

Differences in the magnitude of UV photodegradation among our litter types followed trends in the initial C:N ratio of litter. Specifically, RR_{UV} and C:N were lowest in *C. dactylon* and highest in *L. tridentata* leaves (Table 3). Similarly, King et al. (2012) found that the relative contribution of UV photodegradation to mass loss was positively correlated with the initial C:N ratio of litter. High C:N ratios are indicative of lower N availability and hence lower microbial decomposition, which may in turn increase the relative contribution of photodegradation. It is possible that the positive correlation between UV photodegradation and litter C:N ratio could be an artifact of our experimental approach, and the approach taken in most photodegradation studies. We compared litter mass loss in sunlight to that when UV radiation was excluded and attributed the difference in mass loss to photodegradation. However, excluding UV would not only prevent UV photodegradation, but could increase microbial decomposition and litter mass loss because solar UV reduces the activity of some microbes (Caldwell et al., 2003). This greater microbial decomposition under UV exclusion would reduce treatment differences in mass loss, in turn reducing RR_{UV} values. In low quality, high C:N litter, we would expect microbial decomposition to be more limited by nutrients, such that enhancements in microbial decomposition under UV exclusion would be smaller than those in higher quality litter, leading to higher RR_{UV} values. Hence, higher RR_{UV} in high C:N litter might be a result of lower microbial-

driven mass loss (relative to low C:N litter) when UV is excluded, rather than greater UV photodegradation *per se*. As King et al. (2012) noted, few studies have attempted to minimize microbial activity in conjunction with assessing photodegradation, and this has likely confounded estimates of photodegradation.

When we minimized microbial activity in Experiment 2, we found that the magnitude of solar photodegradation was large. Mass loss of sterilized young and old litter in sunlight was 11.4 and 45.9 times greater than that of shaded litter, respectively (Fig. 6). These RR_{sun} values are much greater than the RR_{uv} values we found in Experiment 1 (1.2-1.4). We suspect that the primary reason they are much greater is not because RR_{sun} considers the effect of both visible and UV, but rather because microbial degradation was minimized in Experiment 2. Supporting this idea, in unsterilized litter, the magnitude of photodegradation was much lower: mass loss of young and old litter in sunlight was only 1.3 and 1.5 times greater than that of shaded litter.

Differences in the magnitude of UV photodegradation among litter types in Experiment 1 were not related to initial litter lignin concentration. Specifically, RR_{uv} was highest in *L. tridentata* leaves, while lignin concentrations were highest in twigs (Table 3). Similarly, King et al. (2012) found that the magnitude of photodegradation was not correlated with initial lignin concentrations. Nonetheless, exposure to sunlight led to lignin losses from *C. dactylon* and *L. tridentata* leaf litter (Fig. 3 a,b). Notably, no losses were detected in shade, highlighting the importance of sunlight in lignin decay and consistent with several other studies (Rozema et al., 1997; Day et al., 2007; Evans et al., 2008; Henry et al., 2008; Austin and Ballaré, 2010). Whether this breakdown of lignin is due to direct photolysis of lignin by sunlight, or indirect photolysis, whereby photons are absorbed by other compounds, is unclear (King et al., 2012). We suspect that the relationship between lignin concentration and photodegradation is confounded by factors such as the location of lignin in relation to internal radiation fluxes and

other compounds, which vary among litter types, and in turn make bulk concentration of lignin a poor predictor of photodegradation.

King et al. (2012) found a positive correlation between the relative contribution of photodegradation to mass loss and envelope surface area:litter mass, which one might expect given that less self-shading of litter (high envelope area:litter mass) would promote photodegradation. In Experiment 1, the mass of litter we placed in envelopes differed among litter types, which would influence self-shading of litter pieces and could affect photodegradation. Envelope area/mass was $16.7 \text{ cm}^2 \cdot \text{g}^{-1}$ (*L. tridentata* leaves), $25 \text{ cm}^2 \cdot \text{g}^{-1}$ (twigs) and $50 \text{ cm}^2 \cdot \text{g}^{-1}$ (*C. dactylon*), and hence negatively related to RR_{UV} which was highest in *L. tridentata* leaves and lowest in *C. dactylon*. We further explored the potential influence of litter self-shading by calculating the total silhouette surface area of litter in envelopes:total litter surface areas in our envelopes; these were 68, 228 and 357 cm^2 for *L. tridentata* twigs, *C. dactylon* and *L. tridentata* leaves, respectively, and did not parallel trends in RR_{UV} . In summary, self-shading of litter did not appear to be an overriding determinant of the differences in photodegradation we observed among litter types in Experiment 1.

Differences in the optical properties of litter could conceivably influence the effectiveness of photodegradation. Litter that absorbs more sunlight might be more prone to photodegradation. However, UV absorbance was similar among initial litter types in Experiment 1 (Table 4). Absorbance of visible radiation was highest in *L. tridentata* twigs, suggesting it was not a strong predictor of photodegradation. Conversely, litter that transmits more sunlight might be more prone to photodegradation since it would likely have higher internal fluxes of radiation. However, transmittance of both UV and visible radiation was highest through *C. dactylon* (Table 4) and photodegradation was lowest in this litter (Fig. 2). While neither absorbance nor transmittance of initial litter appear predictive of photodegradation potential, we suspect that the optical properties of litter change significantly as litter decays and initial optical properties may not be indicative of these changes.

The relative contribution of photodegradation to mass loss increased with litter age. In Experiment 1, RR_{uv} generally increased within each litter type over time (Fig. 2), and in Experiment 2, RR_{sun} was greater in old than young litter (Fig. 7). We suspect that as litter ages, structural and chemical breakdown, particularly of the litter surface, would lead to greater fluxes of radiation reaching internal targets, thereby accelerating photodegradation.

4.3. Effectiveness of different solar wavebands in photodegradation

In Experiment 1, both UV-B and UV-A radiation appeared responsible for photodegradation in all litter types, with solar UV-B responsible for more photodegradation than UV-A. For example, by the end of the experiment, *C. dactylon* litter exposed to full sunlight lost 59% of its mass, but when UV-B was filtered it only lost 52%, and when all UV was filtered it only lost 49% of its mass (Fig. 1). Partitioning the effectiveness of different UV wavebands, UV-B was responsible for 12% of mass loss (i.e. $59-52/59 = 0.12$), and UV-A for 5% of mass loss. In *L. tridentata* leaf litter, UV-B and UV-A exposure was responsible for 18 and 12%, respectively, of the mass loss. In twig litter, UV-B and UV-A exposure was responsible for 16 and 11%, respectively, of the mass loss. Austin and Ballaré (2010) also found that solar UV-B was more effective than UV-A in driving mass loss. They also found that this spectral pattern was consistent with the general absorbance spectrum of lignin, illustrating that lignin may be a direct target of photodegradation, consistent with the lignin losses we observed under sunlight (Fig. 5a, b).

4.4. Relationship between mass loss and ash concentration

We found strong positive correlations between litter mass loss and ash concentration over the course of Experiment 1 (Fig. 5). Positive correlations between mass loss and ash have been observed in the Sonoran (Throop and Archer, 2007, 2009) and Chihuahuan (Brandt et al., 2010; Hewins et al., 2013) Deserts. Explanations for these correlations include that soil may be a vector for microbes, abrade litter surfaces which could facilitate microbial colonization or leaching, or buffer temperature and moisture regimes which could enhance microbial activity

(Throop and Archer, 2007, 2009; Lee et al., 2014; Barnes et al., 2012, 2015). It is possible that these correlations are the result of a loss in litter organic mass over time, while the ash content (i.e. mass-basis) simply remains constant, in turn leading to an increase in ash concentration over time. If true, increases in ash concentration would not involve any increase in soil accumulation. To test for this, we analyzed correlations between organic mass loss and ash content. In all litter type/treatment combinations, ash content was positively correlated with mass loss ($P < 0.0001$; not shown), illustrating that soil did indeed accumulate over time and that increases in ash concentration were not simply the result of declining organic mass. Another possibility is that positive correlations between litter mass loss and ash concentration are the result of soil accumulation over time, but that this soil accumulation is not a causative factor in litter mass loss. While we cannot rule this out, the strong correlations we observed demonstrate that soil film accumulation could be a strong facilitator of litter mass loss, particularly during early stages of decomposition.

Soil films could also slow litter decay, via filtering sunlight before it reaches the litter surface and thus reducing photodegradation (Barnes et al., 2012). Therefore, we expected to find thresholds in ash concentrations, above which litter mass losses would be negligible, in sunlight treatments because soil films would absorb sunlight and reduce photodegradation. While we detected threshold ash concentrations in 5 cases, in only 1 case was this in sunlight (Fig. 6e). In 2 cases, thresholds were found in shaded litter (Fig. 6d,h), demonstrating that reductions in photodegradation were not involved. These threshold responses in shade suggest that soil film accumulation eventually fails to facilitate further decay, possibly because of the recalcitrant nature of remaining litter or because microbial inoculation is no longer limiting. Barnes et al. (2012, 2015) presented a conceptual model of litter mass loss in drylands proposing that as litter ages, the relative magnitude of photodegradation would decline because soil films would reduce photodegradation. Under our experimental conditions this did not appear to be the case; rather, photodegradation increased with litter age. Certainly, experimental

protocols (e.g. litter envelopes) would influence soil accumulation, and our envelopes may have reduced soil accumulation and lessened the influence of soil films.

4.5. Influence of shading on mass loss

Our shading treatment in Experiment 1 had strong effects on litter mass loss (Fig. 1). Shaded litter lost the greatest mass in *L. tridentata* leaf and twig litter throughout the experiment, and for the initial 6 months in *C. dactylon* litter. The most plausible explanation for greater loss under shade is that it improved conditions for microbial activity. The higher N concentration and lower C:N of *L. tridentata* leaves in the shade (Fig. 4b) indicate N immobilization, consistent with greater microbial activity. The most likely explanation for improved microbial activity in the shade is that higher relative humidity (Fig. 3) led to greater moisture availability. Regardless of the mechanism, greater mass loss of litter in the shade versus sun strongly suggests that microbial-driven mass loss in the shade was greater than photodegradation losses in sunlight.

There were large differences in the temporal patterns of mass loss of shaded litter among litter types. Shading initially led to the greatest mass loss in *C. dactylon* litter, but this effect disappeared within 6 months, and by the end of experiment shaded litter had lost considerably less mass (44%) than sunlit litter (59%). In contrast, shaded *L. tridentata* leaf litter lost the most mass (39%), although the differences in losses between shaded and sunlit litter appeared to be narrowing over the experiment. Shaded twig litter also lost the most mass, and the differences in losses between shaded and sunlit litter increased over the entire experiment. Our findings suggest that as litter ages, microbial degradation becomes a weaker driver of mass loss, while photodegradation becomes stronger, and this shift in the relative strength of drivers is very dependent on litter type.

In Experiment 2, mass loss of shaded litter was not faster than sunlit litter, likely because we reduced microbial degradation. Nevertheless, shaded litter did lose 5-6% of its mass in unsterilized treatments (Fig. 6a) illustrating that microbial degradation had likely occurred. This

litter was not exposed to liquid water, and uptake of water vapor by litter was apparently great enough to elicit enough microbial activity for significant litter degradation. This is consistent with findings that water vapor uptake by litter can lead to substantial microbial degradation (Nagy and Macauley, 1982; Dirks et al., 2010). Given that high relative humidity was uncommon during the experiment (relative humidity was $\geq 60\%$ for only 92 hrs (7.2% of the experiment) and did not exceed 76%), it appears that microbial degradation, in the absence of liquid water, could be an underappreciated driver of litter mass loss in our system.

5. Conclusions

Sunlight was a significant driver of litter mass loss in our system. The magnitude of photodegradation varied among litter types and was greater in litter with higher initial C:N ratios. Whether this was because litter of high C:N was inherently more susceptible to photodegradation, or this litter was less prone to microbial degradation, which would increase the relative magnitude of photodegradation, was unclear. When we reduced microbial degradation in Experiment 2, the relative magnitude of photodegradation increased. Taken together, our findings suggest that assessments of photodegradation may often underestimate photodegradation because radiation exclusion treatments can enhance microbial degradation, thereby lowering the apparent contribution of photodegradation. Although lignin losses often accompanied photodegradation, litter of high initial lignin concentrations was not predisposed to greater UV photodegradation. While photodegradation was a significant driver of mass loss, our findings also illustrated that microbial degradation in our system was appreciable, even in the absence of liquid water. Collectively, our results suggest that as litter aged, microbial degradation became a weaker driver of mass loss, while photodegradation became stronger, and the timing of this shift in the relative strength of drivers depends strongly on litter type.

Acknowledgements

We thank M. Bliss, M.L. Krieg, J. Halley, L. Stallcop, A. Jones, M. Khan, M. Gross, V. Fargo, B. Pizzoferrato, D. Rios, J. Zatkovich, and N. Appel at ASU for their assistance in sample preparation, collection and analyses, K. Kiecker and B. Wozniak at MSU for assistance in chemical analyses, J.R. McAuliffe for access to the Conservation Area at the Desert Botanical Garden, and an anonymous reviewer for useful comments. This work was supported by NSF DEB-1256180 to TAD and DEB-1256129 and DOE DE-FG36-08GO88156 to CTR.

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852

Table 1. ANOVA of litter mass remaining over Experiment 1.

Source	df	<i>F</i>	<i>P</i>
Time	3	778.1	<0.0001
Litter type	2	808.6	<0.0001
Sunlight	3	57.7	<0.0001
Time x Litter type	6	73.4	<0.0000
Time x Sunlight	9	4.0	0.0001
Litter type x Sunlight	6	23.6	<0.0001
Time x Litter type x Sunlight	18	3.7	<0.0001

Table 2. Litter decay constants (k) and coefficients of determination (r^2) in Experiment 1. Decay constants were estimated by fitting a single exponential model on all mass loss data ($n=50$) for each litter type by treatment combination. All correlations were significant ($P<0.0001$).

Litter type	Treatment	Decay constant (k (y^{-1}))	r^2
<i>C. dactylon</i>	Sunlight	0.74	0.93
	No UV-B	0.64	0.94
	No UV	0.59	0.92
	Shade	0.49	0.88
<i>L. tridentata</i> leaves	Sunlight	0.34	0.85
	No UV-B	0.28	0.90
	No UV	0.23	0.88
	Shade	0.42	0.74
<i>L. tridentata</i> twigs	Sunlight	0.18	0.91
	No UV-B	0.15	0.88
	No UV	0.13	0.84
	Shade	0.25	0.78

Table 3

Table 3. Initial chemistry and area/mass of litter in Experiment 1. Values are means (SE; $n=10$). Values followed by a different letter in a row are significantly different ($P<0.05$).

Parameter	Litter type		
	<i>C. dactylon</i>	<i>L. tridentata</i> leaves	<i>L. tridentata</i> twigs
C (%)	42.4 (0.1) ^a	46.9 (0.6) ^b	47.6 (0.1) ^b
N (%)	2.6 (0.1) ^a	1.6 (0.1) ^b	2.1 (0.1) ^c
C:N	16.1 (0.1) ^a	28.9 (0.9) ^b	22.5 (0.3) ^c
Lignin (%)	7.4 (0.2) ^a	8.8 (0.2) ^b	13.5 (0.8) ^c
Cellulose (%)	38.0 (3.9) ^a	14.6 (1.6) ^b	17.9 (0.8) ^c
Lignin:N	2.8 (0.2) ^a	5.4 (0.7) ^b	6.4 (0.7) ^c
Cellulose:Lignin	4.8 (0.8) ^a	1.7 (0.1) ^b	1.3 (0.1) ^c
Ash (%)	9.4 (0.8) ^a	9.8 (1.8) ^a	5.0 (0.4) ^b
Litter area:mass (cm ² · g ⁻¹)	114.1 (6.5) ^a	59.5 (3.2) ^b	16.9 (2.5) ^c

Table 4. UV and visible absorbance (α) and transmittance (t) of initial litter. Values, shown as percentages, are means (SE; $n=4$). Different letters across a row denote significant differences ($P<0.05$).

Parameter	Litter type		
	<i>C. dactylon</i>	<i>L. tridentata</i> leaves	<i>L. tridentata</i> twigs
α_{300}	95.7 (0.2) ^a	96.1 (0.3) ^a	97.1 (0.1) ^a
α_{350}	94.4 (0.4) ^a	95.8 (0.2) ^a	96.9 (0.2) ^a
α_{400}	81.9 (0.1) ^a	96.0 (0.1) ^b	96.4 (0.2) ^b
α_{450}	63.0 (1.0) ^a	91.5 (0.6) ^b	93.9 (0.3) ^b
α_{500}	50.4 (1.0) ^a	82.2 (1.6) ^b	90.1 (0.5) ^c
t_{300}	0.2 (0.1) ^a	0.0 (0.1) ^a	0.0 (0.1) ^a
t_{350}	0.5 (0.1) ^a	0.0 (0.1) ^b	0.0 (0.1) ^b
t_{400}	5.6 (0.6) ^a	0.0 (0.1) ^b	0.0 (0.1) ^b
t_{450}	12.2 (1.1) ^a	0.0 (0.1) ^b	0.0 (0.1) ^b
t_{500}	16.3 (1.3) ^a	0.1 (0.1) ^b	0.0 (0.1) ^c

Table 5

Table 5. Average temperature of litter in the two envelope treatments, and adjacent free litter, over Experiment 2. Values are means (SE; $n=3$). Values followed by a different letter in a row are significantly different ($P<0.05$).

Litter type and time period	Treatment litter temperature (°C)		
	Sunlight	Shade	Free litter
Young litter			
Diel	32.6 (0.6) ^a	31.8 (0.6) ^{ab}	29.9 (0.7) ^b
Diurnal	37.2 (0.9) ^a	35.8 (0.8) ^{ab}	34.3 (0.9) ^b
Nocturnal	21.8 (0.4) ^a	21.9 (0.3) ^a	20.6 (0.4) ^b
Old litter			
Diel	33.1 (0.7) ^a	32.3 (0.6) ^{ab}	31.2 (0.6) ^b
Diurnal	38.4 (0.9) ^a	37.2 (0.8) ^{ab}	35.9 (0.8) ^b
Nocturnal	22.1 (0.4) ^a	22.3 (0.3) ^a	20.8 (0.4) ^b

Figure legends

Fig. 1. Mass remaining (with mass loss on the right-axes) of (a) *C. dactylon*, and *L. tridentata* (b) leaf and (c) twig litter over Experiment 1. Note that different vertical scales are used for each litter type. Values are means ($\pm$ SE, $n=10$). Final mass remaining with different letters within a panel are significantly different ($P<0.05$).

Fig. 2. Solar UV (a) and UV-B (b) response ratio of mass loss, calculated as the ratio of mass loss in sunlight to mass loss with no UV or UV-B, over Experiment 1.

Fig. 3. Average monthly diel, diurnal and nocturnal air temperature (a-c) and relative humidity (d-f) in litter envelopes of each treatment from January through June 2008 in Experiment 1. Temperature values are means ($\pm$ SE, $n=5$ sensors); treatment bars with different letters within a month are significantly different ($P<0.05$). Relative humidity values are means ($n=1$ sensor).

Fig 4. Initial and final concentrations of C and N, and C:N ratios in (a) *C. dactylon*, *L. tridentata* (b) leaf and (c) twig litter in Experiment 1. Values are means ($\pm$ SE, $n=10$). Bars with different letters within a panel are significantly different ($P<0.05$).

Fig. 5. Final mass of lignin and cellulose, expressed as % of initial mass of these compounds, in (a) *C. dactylon*, *L. tridentata* (b) leaf and (c) twig litter in Experiment 1. Values are means ($\pm$ SE, $n=10$). Bars with the letter “a” are not significantly different from initial (100%); bars with different letters within a panel are significantly different ($P<0.05$).

Fig. 6. Mass remaining versus ash concentration in (a-d) *C. dactylon*, and *L. tridentata* (e-h) leaf and (i-l) twig litter in Experiment 1. Lines are linear regressions. Piecemeal linear regression analysis identified discontinuities (i.e. thresholds) in five cases (panels c, d, e, g, h). All correlations were significant ($P<0.0001$).

Fig. 7. Mass remaining of *L. tridentata* leaf litter at the end of Experiment 2 for (a) all treatment combinations, (b) main treatment effects, and (c) significant interactions. Values are means ($\pm$

SE). Values of RR_{sun} (mass loss in sun/mass loss in shade) are given in panel (a), while ANOVA F -ratios and significance levels are given in panels (b) and (c).

Figure 1

Figures

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7