JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 114, G02004, doi:10.1029/2008JG000772, 2009

Photochemically induced carbon dioxide production as a mechanism for carbon loss from plant litter in arid ecosystems

L. A. Brandt,[1] C. Bohnet,[2] and J. Y. King[1,3,4]

Received 30 April 2008; revised 31 December 2008; accepted 26 January 2009; published 11 April 2009.

[1] We investigated the potential for abiotic mineralization to carbon dioxide (CO_2) via photodegradation to account for carbon (C) loss from plant litter under conditions typical of arid ecosystems. We exposed five species of grass and oak litter collected from arid and mesic sites to a factorial design of ultraviolet (UV) radiation (UV pass, UV block), and sterilization under dry conditions in the laboratory. UV pass treatments produced 10 times the amount of CO_2 produced in UV block treatments. CO_2 production rates were unaffected by litter chemistry or sterilization. We also exposed litter to natural solar radiation outdoors on clear, sunny days close to the summer solstice at midlatitudes and found that UV radiation (280–400 nm) accounted for 55% of photochemically induced CO_2 production, while shortwave visible radiation (400–500 nm) accounted for 45% of CO_2 production. Rates of photochemically induced CO_2 production on a per-unit-mass basis decreased with litter density, indicating that rates depend on litter surface area. We found no evidence for leaching, methane production, or facilitation of microbial decomposition as alternative mechanisms for significant photochemically induced C loss from litter. We conclude that abiotic mineralization to CO_2 is the primary mechanism by which C is lost from litter during photodegradation. We estimate that CO_2 production via photodegradation could be between 1 and 4 g C m^{-2} a^{-1} in arid ecosystems in the southwestern United States. Taken together with low levels of litter production in arid systems, photochemical mineralization to CO_2 could account for a significant proportion of annual carbon loss from litter in arid ecosystems.

Citation: Brandt, L. A., C. Bohnet, and J. Y. King (2009), Photochemically induced carbon dioxide production as a mechanism for carbon loss from plant litter in arid ecosystems, *J. Geophys. Res.*, *114*, G02004, doi:10.1029/2008JG000772.

1. Introduction

[2] Decomposition is the primary process by which carbon and nutrients are cycled between plants, soil, and the atmosphere. Therefore, understanding controls on litter decomposition is essential to understanding the global carbon (C) cycle. While extensive research on litter decomposition in a variety of ecosystems has elucidated the factors that contribute to global variation in decomposition and nutrient cycling [*Gholz et al.*, 2000; *Parton et al.*, 2007], decomposition in arid ecosystems does not fit these global patterns, occurring more rapidly than predicted by precipitation and temperature. As arid ecosystems cover approximately one third of Earth's land area [*Deichmann and Eklundh*, 1991], it is important that we understand controls on decomposition in these systems. A growing body of evidence demonstrates that photodegradation, the breakdown of chemical compounds by solar radiation, plays a significant role in the decomposition of surface litter in arid ecosystems [*Austin and Vivanco*, 2006; *Gallo*, 2006; *Brandt et al.*, 2007; *Day et al.*, 2007]. This abiotic process can account for up to 60% of litter mass loss in semiarid systems [*Austin and Vivanco*, 2006]. However, the mechanisms for this mass loss remain unclear. There are several mechanisms by which C could be lost via photodegradation leading to litter mass loss: (1) facilitation of microbial decomposition from changes in litter chemistry; (2) increased leaching losses of dissolved organic matter from changes in litter solubility; and (3) photochemical mineralization of the litter.

[3] One possible explanation for mass loss via photodegradation is that photochemical transformations of organic matter could make litter more available to the decomposer community. Extensive research in aquatic systems has shown that photochemical transformation of dissolved organic matter (DOM) can have negative or positive effects on biological decomposition [see *Wetzel et al.*, 1995; *Amon and Benner*, 1996; *Anesio et al.*, 1999b; *Amado et al.*, 2007]. Research on DOM has found primarily positive effects of photodegradation on microbial decomposition when DOM is plant-derived [*Tranvik and Bertilsson*, 2001]. Therefore, one could hypothesize that effects of

[1]Department of Ecology, Evolution and Behavior, University of Minnesota, St. Paul, Minnesota, USA.
[2]Department of Biology, University of Northern Iowa, Cedar Falls, Iowa, USA.
[3]Department of Soil, Water, and Climate, University of Minnesota, St. Paul, Minnesota, USA.
[4]Now at Department of Geography, University of California, Santa Barbara, California, USA.

0148-0227/09/2008JG000772$09.00

photodegradation on microbial decomposition of terrestrial litter would also be positive.

[4] However, levels of microbial activity in arid systems are relatively low, and recent research in arid and semiarid systems does not support this hypothesis. In a study in a semiarid system in New Mexico, *Gallo et al.* [2006] examined simultaneous effects of photodegradation and exposure to solar radiation on microbial extracellular enzyme activities. Enzyme activity per unit litter mass was unaffected by solar radiation, and effects on enzyme efficiency were positive or negative depending on litter type, suggesting no clear effect through facilitation. *Austin and Vivanco* [2006] observed the same patterns of litter mass loss via photodegradation with and without the addition of biocides in a semiarid steppe. While it is possible that the microbial community was not completely eliminated under field conditions, it was at least significantly reduced, suggesting that effects were not due to microbial facilitation. In addition, *Brandt et al.* [2007] showed that effects of photodegradation were higher under dry conditions when microbial activity was lower. Finally, recent research has shown that exposure to ultraviolet (UV) radiation can have direct negative effects on soil microbial communities in arid ecosystems [*Belnap et al.*, 2008]. Therefore, it seems likely that the primary mechanism by which photodegradation increases litter mass loss in arid ecosystems is abiotic.

[5] There are two major abiotic mechanisms for C loss via photodegradation: increased leaching losses and photochemical mineralization. First, photochemical transformation of organic molecules in the litter can increase litter solubility, leading to increased leaching losses of dissolved organic carbon (DOC) [*Gehrke et al.*, 1995; *Vähätalo et al.*, 1998; *Anesio et al.*, 1999b; *Gallo et al.*, 2006]. Simultaneous leaching and exposure to solar radiation can lead to increased DOC loss rates from litter up to four times those in the dark [*Vähätalo et al.*, 1998]. It is highly likely that increased leaching via photodegradation accounts for a substantial fraction of the litter mass that is lost in arid systems, as abiotic losses including leaching can account for up to 40% of litter mass loss early in the decomposition process in arid systems [*Vossbrinck et al.*, 1979]. However, it is unclear whether these losses can account for all of the litter mass loss via photodegradation. In addition, linear patterns of decay observed in arid systems [*Austin and Vivanco*, 2006] do not follow the patterns expected if these losses were due to leaching alone. If leaching losses were the primary mechanism, we would expect short periods of rapid mass loss that correspond to large precipitation events. In contrast, a linear pattern of decay would indicate a constant mass loss over time incongruent with large precipitation events.

[6] In addition to leaching losses, photodegradation can lead to mineralization of organic matter to inorganic compounds. Research has demonstrated that carbon monoxide (CO) can be produced by photodegradation of both DOM in water [*Valentine and Zepp*, 1993] and leaf litter in the air [*Tarr et al.*, 1995; *Schade et al.*, 1999]. Recent research also indicates that trace amounts ($7-50$ ng CH_4 g^{-1} h^{-1}) of methane (CH_4) can be released from plant litter in air by photochemical mechanisms [*Vigano et al.*, 2008]. In aquatic systems, however, the majority of inorganic carbon lost via photochemical mechanisms is as dissolved inorganic carbon (DIC, i.e., the sum of inorganic carbon species CO_2, H_2CO_3, HCO_3^{1-}, and CO_3^{2-}) which is estimated to be 20 times greater than CO losses [*Miller and Zepp*, 1995]. In the absence of water, this flux would occur as CO_2. Little is known about the contribution of photodegradation to CO_2 production in terrestrial systems. Only one previous study, using leaf litter of three aquatic macrophyte species, has demonstrated that CO_2 can be produced via photodegradation of dried leaves in the air [*Anesio et al.*, 1999a]. However, the factors controlling rates of photochemical CO_2 production remain unknown.

[7] It is possible that photochemical CO_2 production depends on plant litter chemistry. Research examining the role of photodegradation in litter decomposition in the field has shown that exposure to UV radiation leads to a decrease in litter lignin content [*Rozema et al.*, 1997; *Day et al.*, 2007]. Lignin molecules contain regions that absorb ultraviolet radiation and are well known to be photochemically reactive [see *Moorhead and Callaghan*, 1994, and references therein]. Therefore, one would expect that litter with a higher initial lignin concentration may produce photochemically derived CO_2 at a higher rate. Other evidence suggests that leaf surface area may be a more important driver than litter chemistry [*Anesio et al.*, 1999a; *Gallo*, 2006], as photochemical reactions can only occur on surfaces exposed to radiation. To date, there is insufficient information to determine whether litter chemistry, surface area, or both are important in driving photochemical CO_2 production.

[8] Previous research suggests that ultraviolet as well as visible wavelengths may be responsible for photochemical CO_2 production. *Granéli et al.* [1998] found that ultraviolet (UV, $280-400$ nm) wavelengths accounted for about 56% and photosynthetically active radiation (PAR, $400-700$ nm) accounted for about 44% of DIC production from photodegradation of DOM. This research points out that although UV radiation accounts for a small percentage of the total energy in the solar spectrum (approximately 7%, depending on season), it plays a large role in photochemical reactions. Research on total mass loss of litter in the field shows that wavelengths greater than 320 nm may make an important contribution to photodegradation [*Austin and Vivanco*, 2006]. Further research is needed, however, to clarify whether it is UV-A ($320-400$ nm) or PAR radiation that is driving these patterns and whether these patterns reflect a direct loss of carbon as CO_2.

[9] The objective of our research was to quantify the importance of photochemically induced CO_2 production as a mechanism for litter mass loss in terrestrial ecosystems. We hypothesized that CO_2 production would depend on: (1) litter chemistry, (2) the amount of surface area of litter exposed, and (3) radiation wavelength and intensity. We hypothesized that photochemically induced CO_2 production would be higher from litter with higher lignin concentrations and that production would increase with the proportion of surface area exposed. We hypothesized that photochemical production of CO_2 from litter in air would depend on both ultraviolet and visible wavelengths of radiation and that these fluxes should increase with increasing radiation dose. In order to test our hypotheses, we conducted a series of controlled experiments under natural and artificial radiation conditions to measure photochemically derived CO_2. In addition, we investigated the relative importance of this

Table 1. Initial Litter Chemistry Characteristics of Plant Litters Used in Experiments[a]

Species	Origin	Code	Cell Solubles (%)	Hemi-cellulose (%)	Cellulose (%)	Lignin (%)	C (%)	N (%)	C:N
Andropogon gerardii	Minnesota	ange	12.7 (0.5)	34.2 (0.2)	44.6 (0.4)	9.0 (0.2)	46.4 (0.3)	0.36 (0.01)	130
Bouteloua eriopoda	New Mexico	boer	21.2 (0.1)	38.3 (0.3)	33.1 (0.3)	8.0 (0.3)	44.1 (0.2)	0.60 (0.00)	73.6
Bouteloua gracilis	Minnesota	bogrM	19.9 (0.3)	41.9 (0.2)	30.1 (0.4)	8.6 (0.5)	45.5 (0.6)	1.04 (0.02)	43.6
Bouteloua gracilis	New Mexico	bogrN	17.7 (0.1)	34.5 (0.1)	42.2 (0.3)	6.2 (0.2)	43.2 (0.2)	0.35 (0.00)	125
Quercus ellipsoidalis	Minnesota	quel	41.2 (0.3)	17.0 (0.4)	17.7 (0.7)	24.6 (0.2)	49.7 (0.1)	0.86 (0.00)	57.8
Quercus macrocarpa	Minnesota	quma	52.6 (0.3)	15.4 (0.18)	17.9 (0.2)	14.7 (0.1)	46.9 (0.4)	0.69 (0.1)	68.4

[a]Means (n = 3) and standard error shown.

mechanism compared to increased C losses from leaching and microbial facilitation.

2. Methods

2.1. Litter Collection and Preparation

[10] The primary purpose of our experiments was to elucidate the mechanisms by which carbon could be lost via photodegradation in arid ecosystems. As a representative arid system, we chose Chihuahuan Desert Grassland at Sevilleta National Wildlife Refuge (NWR), New Mexico (34.21°N, 106.41°W). The site receives high levels of radiation owing to its high elevation (1600 m), low cloud cover, and low-statured vegetation. It is dominated by *Bouteloua gracilis* and *Bouteloua eriopoda*, two short, C-4 grasses. We collected standing dead litter from these two dominant species in March, dried it in paper bags, and shipped it to the University of Minnesota, St. Paul Campus (44.93°N, 93.05°W) for our experiments. As a secondary question, we were interested in understanding controls of litter chemistry on photochemical CO_2 production. To address this question, we collected litter locally in Minnesota to encompass a wide range of litter chemistries. We chose two oak species, *Quercus macrocarpa* and *Quercus ellipsoidalis*, and two grass species, *Andropogon gerardii* and *Bouteloua gracilis*. We collected freshly fallen oak litter locally in St. Paul in October and air-dried it in paper bags. We collected grass litter from planted monocultures located in Princeton, Minnesota, United States (45.61°N, 93.58°W) in late October following senescence. Because the litter was slightly damp upon collection, we immediately oven-dried it at 35°C for 7 days or until it reached a constant weight. We collected *B. gracilis* litter from both New Mexico and Minnesota to test whether conditions under which litter was grown had any effect on photochemical CO_2 production.

[11] We sorted the litter by species and removed seed heads, roots, and any other extraneous material so that only leaf and stem material remained for our experiments. We then coarsely ground each species through a Thomas-Wiley Minimill (Thomas Scientific, Swedesboro, New Jersey, United States) to pass through a 2 mm screen and homogenized the material by shaking. We ground the litter to standardize for differences in leaf shape among species and obtain a relatively flat surface for exposure in our microcosms. It is possible that grinding might have affected the photoreactivity of the litter, but we assumed this effect was minimal. We determined differences between species in initial litter fiber characteristics using the forage fiber technique [*Van Soest*, 1967]. Ground samples (1 mm mesh) were subjected to sequential acid digestions to quantify cell solubles, hemicellulose, cellulose, and lignin concentrations using an ANKOM fiber analyzer (ANKOM Technology, Macedon, New York, United States). We further ground subsamples of initial litter to a powder by ball milling and analyzed for total C and N using an elemental analyzer (Elementar, Mt. Laurel, New Jersey). Litter differed in initial chemistry, especially between oak and grass species (Table 1).

2.2. Experiment 1: Species Effects on Carbon Dioxide Fluxes Over 10 Weeks

[12] In our first experiment, we addressed the effects of litter type, sterilization, UV exposure, and exposure time on photochemically induced CO_2 fluxes using microcosms in the lab. We designed microcosms following the design of *Gehrke et al.* [1995]. Wide-mouth glass canning jars (Mason jars; either 500 ml or 250 ml depending on the experiment) were fitted with 8 cm diameter, 0.32 cm thick clear plastic lids made of either UV-transparent acrylic (UV pass, which passes 90% of all wavelengths of radiation, including UV-A and UV-B, Solacryl SUVT®, Spartech Polycast, Stamford, Connecticut, United States) or polycarbonate (UV block, which passes 90% of PAR but eliminates 90% of UV-A and UV-B, optically equivalent to Lexan XL-1®, GE, Pittsfield, Massachusetts, United States). The sides of the microcosms were covered on the outside with aluminum foil to eliminate diffuse radiation from the sides. A small butyl rubber septum was fitted at the edge of each lid for headspace sampling. After the jars were filled with litter, lids were sealed to the jars with clear silicone caulk and allowed to cure for at least 24 h prior to the experiments. The caulk was protected from light exposure with jar lid rings. When the silicone had cured, we flushed the jars with a high-purity compressed air mixture (Scott Specialty Gases, Plumsteadville, Pennsylvania, United States) that closely resembled ambient outside air in order to eliminate volatile organic compounds released from the silicone during the curing process and to obtain a consistent atmosphere among microcosms. To account for any photodegradation of the plastic materials used in the design, empty microcosms of both UV treatment types containing no litter were included as blank controls.

[13] To eliminate microbial activity, we sterilized half of the dried, ground litter by autoclaving at 121°C for 30 min. The litter was immediately removed from the autoclave upon completion of the cycle and placed in a drying oven at 55°C. We chose autoclaving to avoid any confounding effects chemical biocides may have on the photodegradation process. To determine the effectiveness of autoclaving over several weeks, we set up a factorial experiment of sterili-

zation (autoclaved and un-autoclaved) and litter species (*A. gerardii* and *B. gracilis*) and placed the litter on trays in a constant temperature room (20°C) for 3 weeks. After the 3-week period, we determined bacterial and fungal colonization by extracting 150 mg litter in 100 ml of sterile DI water for 30 min followed by serial dilution plating on oatmeal agar that contained either a fungicide (cyclo-poly-pen) or bactericide (novobiocin). Although culturing presents a biased view of the microbial community, we believe that this method was a good proxy for determining the effectiveness of sterilization. We counted colony-forming units (CFUs) after incubation at 25°C for 3 days. Microbial colonization was not observed in autoclaved litter even after 3 weeks, and autoclaving was determined to be an effective sterilization method.

[14] We filled each microcosm with 1 g of one of the six litter types described above (1 g was the minimum to completely cover the bottom of the jar). A full factorial of litter type, sterilization, and UV treatment (UV block, UV pass) was arranged in a randomized incomplete block design. Three replicates of each factorial combination plus blank controls (78 microcosms total) were placed 25 cm below twelve Q-panel UV-A 340 lamps (Cleveland, Ohio, United States; hereafter, referred to as UV lamps) in a constant temperature room (20°C) and irradiated continuously for a 10-week period. The UV lamps have a peak emission at 340 nm, with cutoffs at 295 and 400 nm, closely following the UV portion of the solar spectrum. We chose these lamps because they have been used previously in similar studies [*Anesio et al.*, 1999a] and are effective for irradiating a large number of samples simultaneously. The disadvantage of these lamps is that they emit minimal amounts of PAR, which has been shown to be important in photodegradation of DOM [*Granéli et al.*, 1998; *Anesio et al.*, 1999a]. We measured spatial variation in radiation received by measuring broadband UV-A and UV-B using a UV radiometer (UV-X, UV Products, Upland, California, United States) with separate sensors. The UV-B sensor (UVX-31) was calibrated at 310 nm with a spectral response curve encompassing 260–370 nm. The UV-A sensor (UVX-36) was calibrated at 365 nm with a spectral response curve encompassing 300–400 nm. Samples were placed only in the areas that were determined to be spatially uniform and received approximately 5 W m^{-2} UV-B and 9 W m^{-2} UV-A, which corresponds to radiation intensity levels measured on the rooftop at both midmorning and midafternoon on clear, sunny days near the summer solstice in St. Paul, Minnesota.

[15] We also monitored temperature every 2 h by placing small data-logging temperature sensors (Ibutton, Maxim Integrated Products, Sunnyvale, California) in the empty control jars to determine whether the lids affected temperature differently. We did not place the temperature sensors in the jars with litter as the sensors would have partially blocked the litter from solar radiation. It is possible that temperatures in the empty jars differed slightly from jars with litter, as litter would change the absorption of solar radiation. However, we would expect this effect to be the same under both UV treatments.

[16] Prior to being placed under the lamps and at each sample date, a 7 ml headspace sample was collected from each jar and injected into a gas chromatograph (GC, Shimadzu 14-A, Kyoto, Japan) with a thermal conductivity detector to analyze for CO_2 concentration. Headspace was sampled after 24 h then approximately every 2 to 3 days for the first 3 weeks, and approximately once weekly thereafter. In total, microcosms were sampled 15 times over the 10-week period. CO_2 concentrations were calculated using a standard curve generated from five CO_2 standards (Airgas, Radnor, Pennsylvania) that bracketed the range of concentrations observed from our samples. We determined the mass of C lost as CO_2 by converting CO_2 concentration to grams CO_2-C using the ideal gas law and measurements of ambient environmental conditions. We allowed CO_2 to accumulate in the headspace in order to more easily discern differences between treatments, as fluxes were relatively low. We flushed the jars once over the 10-week period (at 7 weeks) in order to determine whether the accumulation of photoproducts in the headspace was affecting rates of CO_2 accumulation over time. At the end of the 10-week period, we also analyzed headspace for methane (CH_4) accumulation using a GC fitted with a flame ionization detector.

[17] At the end of the experiment, we weighed the litter to determine any mass loss not attributable to CO_2. We then examined treatment effects on leaching losses of C and N. A 100 mg subsample from each microcosm was leached in 50 ml sterile tap water for 24 h at 4°C. We used tap water as it more closely resembles the ionic concentration of natural rainwater. After the 24-h period, the leachate was passed through a precombusted Whatman GF/F filter and kept frozen prior to analysis on a total organic carbon/total nitrogen autoanalyzer (Shimadzu TOC-V_{CPN}). We analyzed our leached samples and tap water blanks for total nonpurgeable organic carbon and total nitrogen. We did not analyze samples from before the experiment because all samples were taken from the same pool prior to the experiment, and we were only interested in treatment effects. Average TOC/TN concentration in the tap water was subtracted from the samples prior to statistical analysis.

2.3. Experiment 2: Effects of Wavelength and Radiation Intensity

[18] In a second experiment, we determined which wavelengths were responsible for photochemically induced CO_2 production using natural radiation on the roof of our building at the University of Minnesota, St. Paul Campus (44.93°N, 93.05°W). We selected clear sunny days close to the summer solstice (21 June) in order to estimate the maximum potential for photodegradation in the region. For this experiment, we used 2 g sterilized litter of *B. gracilis* collected in Minnesota. We filled 250 ml wide-mouth jars with 2 g of litter. We chose smaller jars than in the previous experiment in order to reduce shading from the sides. All jars were fitted with UV pass lids as described above. In order to manipulate wavelength, we added cutoff filters above the lids that blocked all radiation below a specific wavelength (Figure 1). In one trial, we used filters to determine the relative importance of UV-A, UV-B, and PAR. Three replicates of microcosms with and without litter were used for each wavelength range. Each microcosm without litter also contained a temperature data logger as in the previous experiment. Microcosms were placed on the

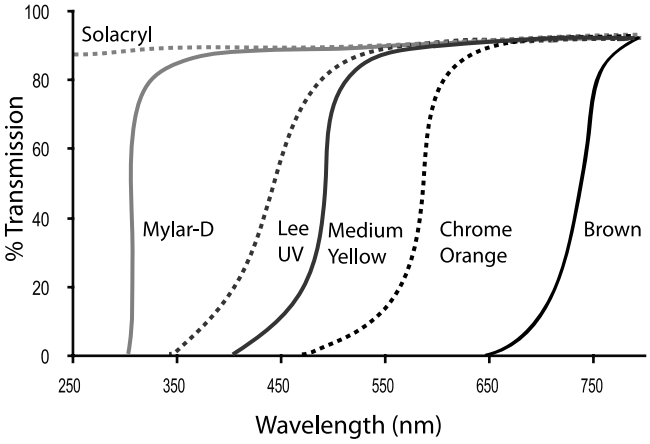

Figure 1. Transmission (%) of different filters used in experiment 2 versus wavelength. Solacryl-SUVT (Spartech Polycast, Stamford, Connecticut, United States) was used as a lid for all microcosms. Additional films were placed on top of the lids to block UV-B (Mylar-D, DuPont, Wilmington, Delaware, United States), UV-A (Lee UV), or 100 nm PAR wave bands (medium yellow, chrome orange, brown, Lee Filters, Burbank, California, United States).

roof for a 3-day period of consecutive clear sunny days from 29 June to 1 July 2007. Microcosm headspace samples were collected at 0, 24, 48, and 72 h and were analyzed for CO_2 concentration on the GC as described above. Ambient solar radiation was monitored continuously using a broadband pyranometer (Licor, Lincoln, Nebraska, United States). Mean solar radiation for that period was 28 MJ m^{-2} d^{-1}. We also measured UV-A and UV-B periodically to compare to experiment 1 above. After determining that PAR made a large contribution to photochemically induced CO_2 flux, we conducted a second trial using additional cutoff filters to manipulate 100 nm wave bands within the PAR range at a later clear sunny day (12 July). Solar radiation for this day was 20 MJ m^{-2} d^{-1}.

2.4. Experiment 3: Influence of Litter Density on CO_2 Fluxes

[19] We hypothesized that only litter that was directly exposed to solar radiation would produce photochemically derived CO_2. Therefore, as litter density increased, we expected that the amount of photochemically induced CO_2 production per unit mass of litter would decrease. To test this hypothesis, we filled 500 ml jars with 1, 2, 3, 4, and 5 g of sterile *B. gracilis* litter collected in Minnesota, which corresponded to litter densities of approximately 260, 520, 780, 1040 and 1300 g m^{-2}, respectively. The lower bound of litter density (260 g m^{-2}) was chosen because this was the minimum density required to completely cover the bottom of the jar, ensuring a consistent surface area across samples. Three replicates of each density treatment were fitted with either UV pass or UV block lids as described above, with three replicate empty microcosms of each radiation treatment as a control. We placed litter under UV lamps as in experiment 1 and measured CO_2 accumulation in microcosm headspace four times over a 17-day period as described previously.

2.5. Experiment 4: Facilitation of Microbial Decomposition

[20] We examined whether photodegradation of litter would facilitate subsequent heterotrophic decomposition by measuring soil respiration after pretreated litter was buried in the soil. This design was similar to experiment 1 above using a factorial design of litter type, sterilization, and preirradiation, but was carried out using a separate set of samples. For this experiment, we used only 2 litter species (*A. gerardii* and *B. gracilis*) because of space constraints under the lamps. The sterilization treatment was used to tease apart direct effects of photodegradation from UV effects on the microbial community present on the litter prior to burial. We placed coarsely ground litter on shallow trays (30 by 40 cm) at a density of 65 g m^{-2} in order to maximize exposure of the litter to UV radiation. Half of the trays were placed under UV lamps (UV irradiated), while the other half were placed on an identical shelf without lamps (dark). Both UV irradiated and dark treatments were placed in the same constant temperature room (20°C) for 3 weeks. Although the two treatments were spatially separated, we felt the confounding effects of spatial separation were minimal compared to that of covering the dark treatment under the lamps, which could result in excess heating. Litter on each tray was mixed every 2 days, and trays were rotated to a different position on the shelf in order to ensure even exposure. After 3 weeks, 3 subsamples of each litter treatment were analyzed for effects on bacterial and fungal CFUs as described previously.

[21] Seven subsamples (100 mg) of each pretreated litter type were each placed in mesh bags (3 × 3 cm) constructed of nylon netting (0.3 mm mesh). Each bag was buried in 150 ml specimen cups containing 25 g air-dry equivalent sieved soil (2 mm) collected from the top 10 cm at Sevilleta NWR (New Mexico). Soil was preincubated at 60% water holding capacity for 3 weeks in order to conduct this experiment without the effect of soil C release owing to re-wetting. The specimen cups containing soil amended with litter were incubated in 500 ml jars in the dark at 20°C for 21 days. We added water as needed to main constant soil moisture. We estimated respiration rates by capping the jars with an opaque lid fitted with a butyl rubber septum and sampling at 0 and 24 h. We followed the same CO_2 analysis procedure as in experiments 1–3. We sampled headspace for CO_2 at 1, 2, 4, 7, 14, and 21 days.

2.6. Statistical Analysis

[22] We determined treatment effects on CO_2 production using repeated measures ANOVA using nonlinear mixed effects (nlme) in R (version 2.4.1, The R Project). Data for each experiment were fit to the best autocorrelation structure on the basis of Akaike's information criterion (AIC). Radiation treatment, sterilization treatment, and litter type were treated as fixed effects, while time and block were treated as random effects. Since we found no time by treatment interactions, we analyzed the cumulative CO_2-C produced using a 3-way ANOVA in JMP (SAS Institute, Cary, North Carolina, United States) eliminating time as a factor. For abiotic CO_2 fluxes, we calculated rates of CO_2 production as mg CO_2-C m^{-2} d^{-1} (see Results, experiment 3 for justification). For experiment 4, we calculated cumulative C respired by interpolating rates in between sampling

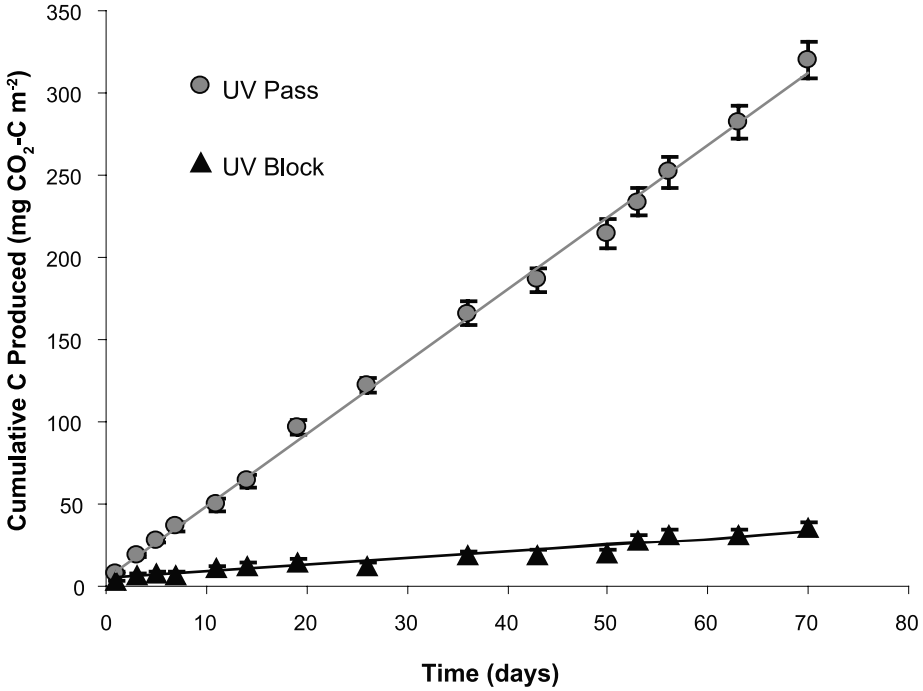

Figure 2. Cumulative CO_2-C produced in microcosms containing 1 g of dry plant litter during the 10-week incubation. Data were averaged across species and sterilization treatment as no significant effects were found for those treatments. Any outliers that were later determined to have been caused by leaks were eliminated from the analysis (n = 26 (UV pass), n = 24 (UV block)). Bars represent standard error. Linear regression estimate for UV pass: C = 4.98 + 4.39t; adjusted r^2 = 0.91, $p < 0.0001$; UV block: C = 4.63 + 0.41t; adjusted r^2 = 0.37, $p < 0.0001$. C, cumulative CO_2-C produced; t, time.

periods. Cumulative C respired was then analyzed by 3-way ANOVA in JMP.

3. Results

3.1. Experiment 1: Species Effects on CO_2 Fluxes Over 10 Weeks

[23] CO_2 flux rates for litter in the UV pass treatment were approximately 10 times those in UV block treatment ($p < 0.0001$; see Figure 2). Fluxes of CO_2 from UV pass litter averaged 4.4 mg CO_2-C m^{-2} d^{-1}. A small amount of CO_2 production was observed in the UV block treatments for both sterile and nonsterile litter (0.4 mg CO_2-C m^{-2} d^{-1}), but this was not significantly different from blank controls. After subtracting the CO_2 produced in the UV block treatments, CO_2 production in the UV pass treatments averaged 4 mg CO_2-C m^{-2} d^{-1}. CO_2 concentrations increased linearly with time over the 10-week period, fitting a pseudo-zero-order decay model (i.e., rates did not decrease with decreasing reactants). No significant differences were observed in cumulative CO_2 production among litter species, litter origin, or sterilization over the 10-week period (Figure 3). *Q. ellipsoidalis* had a slightly higher CO_2 production rate in both treatments, but this was only marginally significant (species effect: p = 0.10). Temperature did not differ significantly between radiation treatments.

[24] Exposure to UV radiation did not affect any additional abiotic pathways that we measured besides CO_2 for C loss from litter. The amount of CH_4 produced in the headspace did not differ significantly between UV treatments (data not shown). Leaching losses of DOC and total N differed among species ($p < 0.0001$; see Figure 4). The highest losses of DOC were from *Q. macrocarpa* and the lowest from *A. gerardii*. Leaching losses of N were greatest from *B. gracilis* litter originating from both Minnesota and New Mexico, United States. However, leaching losses were unaffected by UV radiation exposure, and effects of sterilization were inconsistent across species (Figure 4). We found no detectable change in litter mass after the 10 weeks. The carbon produced over the experimental period would have led to an average mass loss of 0.77 mg from each microcosm, representing less than 0.1% of the 1 g litter used in the experiment. Therefore, the only detectable abiotic C loss we observed was through abiotic mineralization to CO_2.

3.2. Experiment 2: Effects of Wavelength and Radiation Intensity

[25] CO_2 fluxes under ambient radiation on clear days in late June were approximately 4 times greater than under the lamps in the laboratory. Litter under lids that passed all wavelengths of ambient radiation produced an average of 16 mg CO_2-C m^{-2} d^{-1}. Fluxes diminished significantly with the addition of each subsequent cutoff filter, and we observed the greatest decrease when PAR was removed ($p < 0.0001$; see Figure 5). Virtually no CO_2 was produced when a filter that eliminated both PAR and UV was used, and these values did not differ significantly from blank

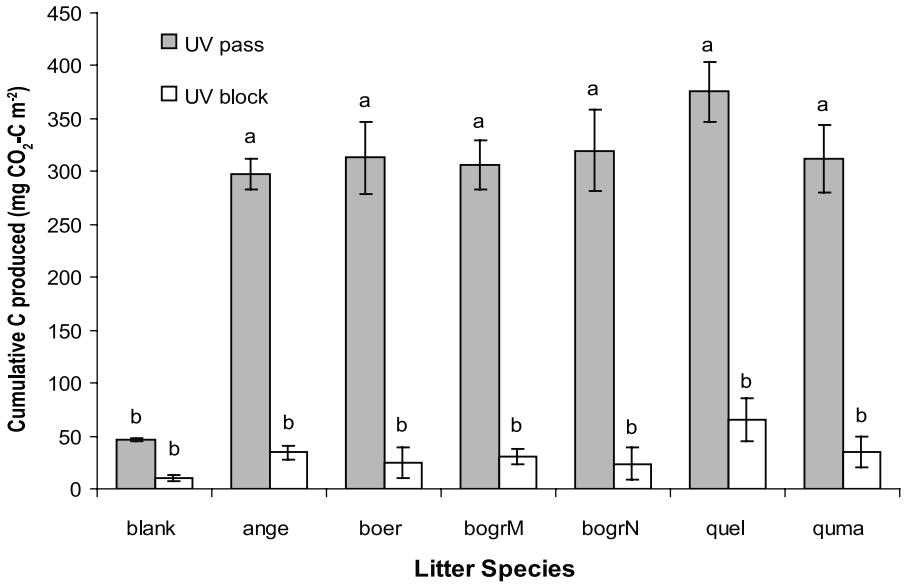

Figure 3. Mean cumulative CO_2-C produced over the 10-week period shown by species and irradiation treatment. Letters indicate significant pair-wise differences (Tukey's HSD). Standard error shown. See Table 1 for species codes.

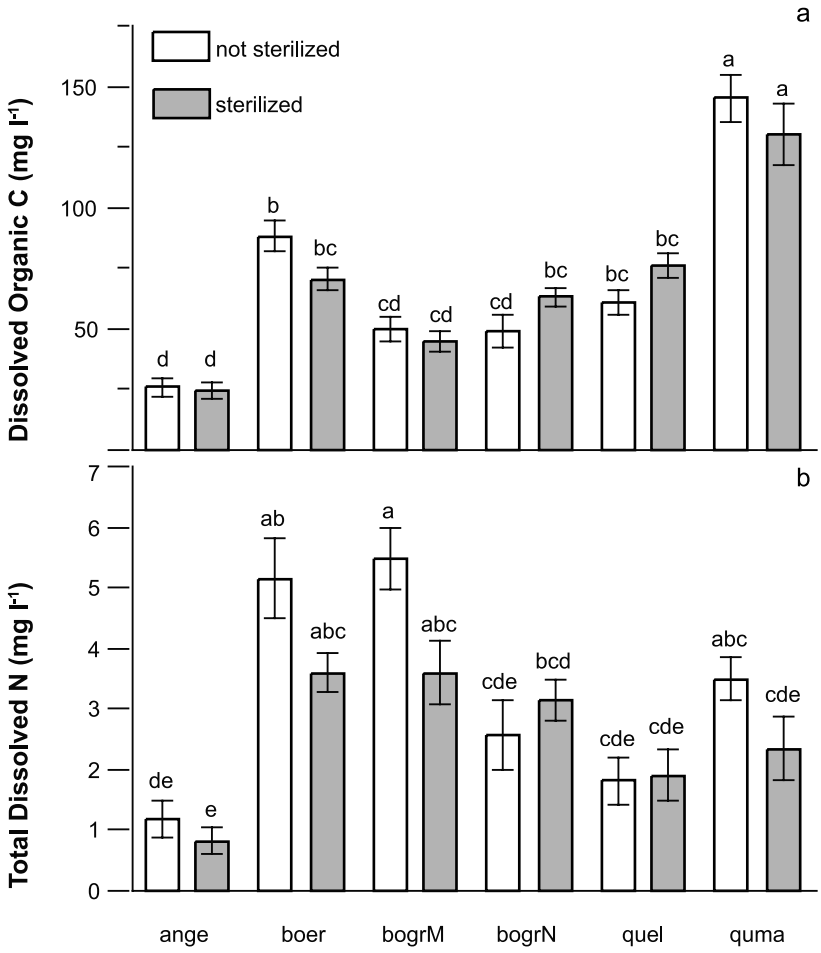

Figure 4. (a) Dissolved organic carbon and (b) total dissolved nitrogen leached from litter, by litter species and sterilization treatment after 10 weeks of irradiation. Exposure to UV radiation had no significant effect on leaching losses. Letters indicate significant pair-wise differences (Tukey's HSD). See Table 1 for species codes.

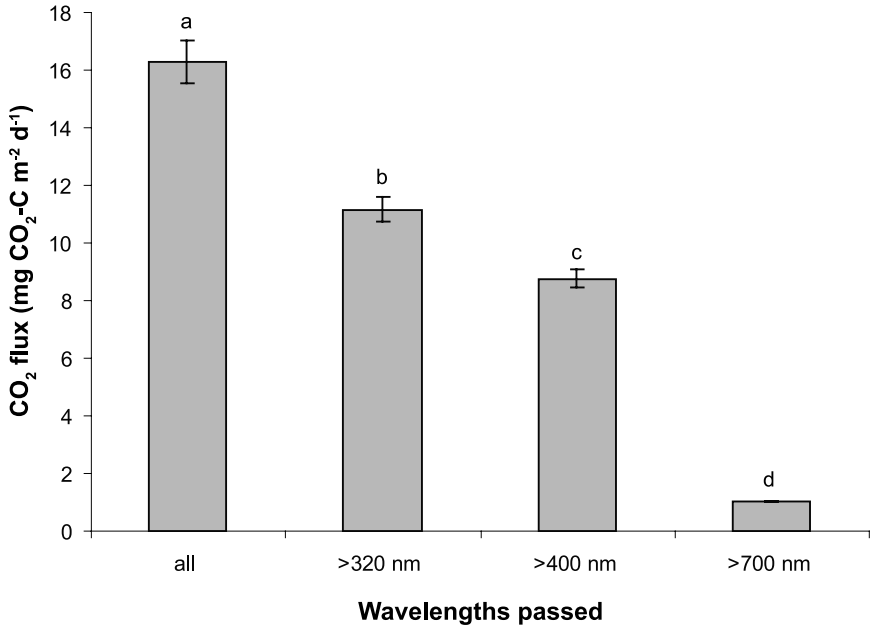

Figure 5. CO_2 fluxes per day under ambient radiation averaged over a 3-day period of clear sunny days from 29 June to 1 July in St. Paul, Minnesota, United States (mean solar irradiance: 28 MJ m^{-2} d^{-1}). Letters indicate significant pair-wise differences (Tukey's HSD). Means (n = 3) and standard error shown.

controls. Further experiments elucidated that shortwave PAR (400–500 nm) was primarily responsible for CO_2 fluxes observed in the PAR range (Figure 6), as a filter cutting off wavelengths less than 500 nm eliminated all detectable CO_2 production. Measurements taken on 12 July showed lower CO_2 production overall, presumably owing to decreases in total radiant energy (20 MJ m^{-2} d^{-1} versus an average of 28 MJ m^{-2} d^{-1} from 29 June to 1 July). When adjusting per unit energy, fluxes were approximately equal across dates at 0.6 mg CO_2-C MJ^{-1}.

[26] Despite the large differences in radiation transmission in the different treatments, mean daily temperature did not differ significantly between treatments. Daily maximum temperature differed by approximately 5°C between our treatment that passed all wavelengths and our treatment that blocked all wavelengths below 700 nm. However, it is

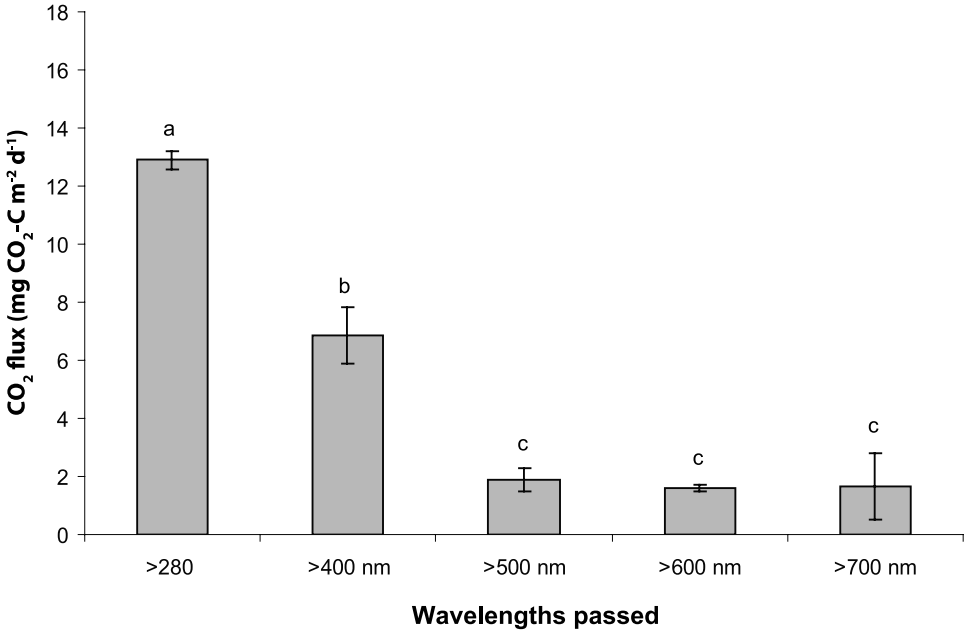

Figure 6. CO_2 fluxes per day under ambient radiation on a clear sunny day (12 July) in St. Paul, Minnesota (solar irradiance: 20 MJ m^{-2} d^{-1}). Different letters indicate significant pair-wise differences (Tukey's HSD). Means (n = 3) and standard error shown.

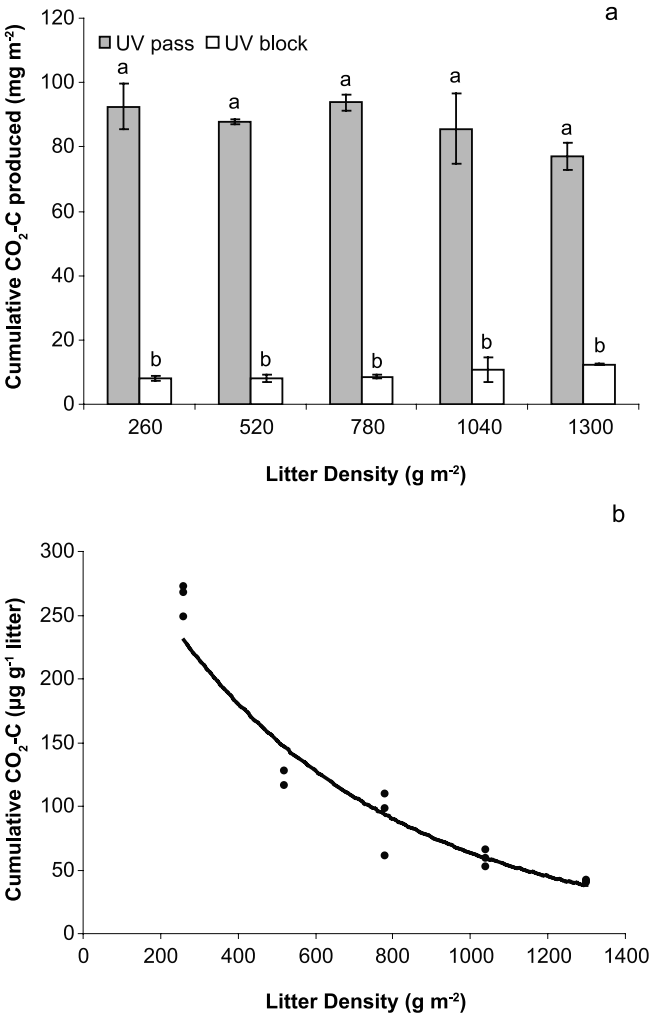

Figure 7. (a) Cumulative CO_2-C produced per meter squared litter under UV pass and UV block treatments for each litter density treatment. The lowest litter density was just sufficient to cover the bottom of the microcosm with a thin layer. Mean (n = 3) and standard error shown. Letters indicate significant pair-wise differences (Tukey's HSD). (b) Cumulative CO_2-C produced per gram litter under the UV pass treatment over a 17-day period versus litter density. Data were fit to an exponential decay model: $y = 362.13 \times e^{-0.0017x}$, $r^2 = 0.9399$, $p < 0.0001$.

unlikely that our results are due to differences in maximum temperature, as temperature decreased linearly with increasing radiation cutoff, while CO_2 fluxes exhibited a sharp decline with exposure to wavelengths longer than 500 nm.

3.3. Experiment 3: Influence of Litter Density

[27] CO_2 fluxes were significantly higher from litter in the UV pass treatment than the UV block treatment for all litter density treatments (Figure 7a). When we calculated CO_2 fluxes on a per unit area basis, we found no significant difference between density treatments (i.e., the slope of the relationship between CO_2 flux and litter density was not different from zero). If we instead calculated fluxes per unit mass, cumulative fluxes of CO_2 per under the UV pass treatment decreased exponentially with increasing litter density (Figure 7b). The intrinsic rate of decay from our samples would be predicted to increase exponentially with decreasing litter mass as long as the litter surface area exposed to radiation remained constant. This is in contrast to microbial decomposition where the intrinsic rate of decay remains constant with decreasing litter mass.

3.4. Experiment 4: Microbial Facilitation

[28] Exposure of unsterilized litter to UV radiation (mixed every 2 days during exposure) significantly reduced the abundance of culturable bacteria and fungi on both *A. gerardii* and *B. gracilis* litter (Figure 8). We found no culturable bacteria or fungi in sterilized litter in either the irradiated or unirradiated litter. When pretreated litter was incubated in soil, cumulative C respired was affected by litter species ($p < 0.0001$) and sterilization ($p < 0.0001$; see Figure 9), but not by prior UV irradiation of the litter. Cumulative C respired in soil amended with litter was greater in microcosms containing *B. gracilis* litter than *A. gerardii* litter. Sterilization decreased the cumulative C respired in both species, presumably owing to the lack of microbial colonization on the litter. However, we did not observe any significant effect of preirradiation on the cumulative C respired from litter of either species.

4. Discussion

[29] Our experimental results indicate that the primary pathway by which C is lost from litter via photodegradation under dry conditions is by direct abiotic mineralization of the litter to produce CO_2. We observed linear rates of CO_2 production from dry litter exposed to UV and PAR radiation and virtually no CO_2 production from dry litter that was not exposed to solar radiation. We did not observe any increase in C losses via leaching or microbial decomposition of litter that had been pre-exposed to UV radiation, nor did we observe any detectable fluxes of methane with exposure to UV radiation.

[30] On the basis of research in aquatic systems, we expected that leaching losses could account for measurable C losses during photodegradation. The fact that we did not observe increased leaching losses with photodegradation may be due to differences in the factors driving aquatic and terrestrial litter decomposition. In aquatic systems, litter is continuously submerged, and leaching and photodegradation occur simultaneously [*Vähätalo et al.*, 1998; *Anesio et al.*, 1999b]. Leaching can also account for the majority of litter mass loss in aquatic systems [*Vähätalo et al.*, 1998], and therefore small increases in DOC loss via photodegradation would be detectable. In contrast, leaching and photodegradation occur asynchronously in arid ecosystems; leaching in arid systems is limited to pulses of precipitation [*Austin et al.*, 2004], which are typically accompanied by a simultaneous decrease in photodegradation from increased cloud cover. Since litter in arid systems is not continuously submerged, leaching also accounts for a small proportion of mass loss, making small differences in DOC losses more difficult to detect. These factors may explain why photodegradation led to negligible DOC losses when litter was photodegraded and subsequently leached in our study and a similar study by *Gallo* [2006].

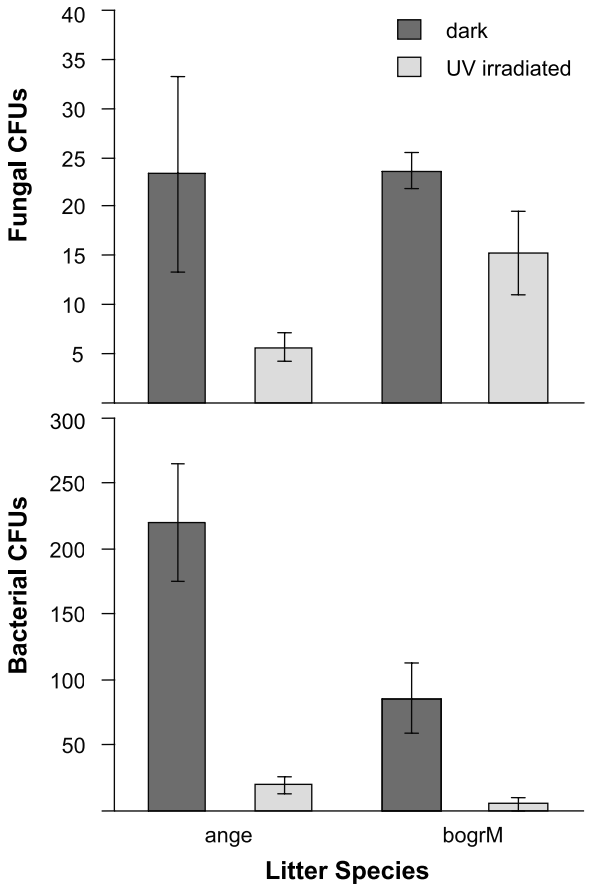

Figure 8. Mean (n = 3) colony-forming units (CFUs) cultured on oatmeal agar from 150 mg litter in 100 ml deionized water that was either exposed to UV radiation or left in the dark. Standard error shown. UV effects were significant for both fungi (p = 0.047) and bacteria (p = 0.001).

[31] In contrast to studies in aquatic systems, we found no evidence that pre-exposure of litter to solar radiation positively or negatively affected subsequent microbial decomposition. Despite a significant reduction in phylloplane fungal and bacterial abundance with exposure to radiation, we did not observe any negative effects on litter decomposition. Recent research has shown that decomposition in the soil is more limited by supply of labile carbon than by microbial abundance [*Kemmitt et al.*, 2008]. However, complete elimination of the microbial community on the leaf surface does appear to have a negative effect on decomposition on the basis of the negative effect of sterilization on respiration observed in our study (experiment 4). Thus, the presence and absence of phylloplane microbes appear to affect C turnover, while differences in abundance do not, at least across the range of abundances examined here. We also did not observe any positive effects of photodegradation on microbial respiration, as we would have expected if photodegradation increased substrate bioavailability. Differences in bioavailability between litter species were apparent and followed established patterns (high C:N, low lignin litter decomposed more quickly). Therefore, any possible differences in microbial respiration induced by photodegradation were orders of magnitude smaller than differences in respiration from interspecific variation in litter chemistry.

[32] We did, however, find strong evidence that photodegradation can lead to abiotic C loss as CO_2. Our study is the first to estimate photochemically derived CO_2 fluxes in the air under ambient solar radiation. Our measurements indicate that fluxes under ambient radiation can be as high as 16 mg m^{-2} d^{-1} at 45°N latitude, and would be expected to be higher in systems at lower latitudes and higher elevations. Mean daily solar radiation for our study was 28 MJ m^{-2} d^{-1}, while maximum daily solar irradiance in the desert southwest can reach 35 MJ m^{-2} d^{-1} or higher [*Moore*, 2003]. Assuming a linear relationship between solar irradiance and a photochemical CO_2 flux of 0.6 mg CO_2-C MJ^{-1} on the basis of our results in experiment 2, we estimate that photochemical CO_2 fluxes in the desert southwest would be 20 mg C m^{-2} d^{-1} on clear, sunny days close to the summer solstice. Even though these fluxes are higher than those measured in our study, they represent a small proportion of total carbon fluxes from soil respiration in arid ecosystems. Even under dry conditions, soil CO_2 fluxes in the desert southwest can average 0.7 g C m^{-2} d^{-1} [*Sponseller*, 2007]. Therefore, CO_2 fluxes from photodegradation in the desert southwest would likely represent a maximum of only about 3% of total CO_2 fluxes from soils when solar radiation is high and soil moisture is low.

[33] While photochemical CO_2 production is a small component of soil CO_2 flux, we examined whether it could represent a significant component of the litter decomposition process. We estimated potential mass loss of litter from photodegradation using the linear relationship between solar irradiance and photochemical CO_2 flux of 0.6 mg CO_2-C MJ^{-1} from our results. For simplicity, we assumed factors such as temperature or moisture would have a minimal effect on this relationship. Yearly ambient solar radiation at Sevilleta NWR (New Mexico) for 2002 (which contained the fewest number of missing days from the data set; see *Moore* [2003]) was 7550.5 MJ m^{-2}. Therefore if we take the product of these two values, we estimate that rates of mass loss as CO_2 from photodegradation would be approximately 4 g C m^{-2} a^{-1}. This is likely an overestimate because it assumes that the soil surface is completely covered by litter and that litter is not shaded by neighboring plants. Shrub cover in the desert southwest can reduce transmission of solar radiation by 42.5–51.2% [*Throop and Archer*, 2007]. Such shading was essentially already accounted for in our study, as solar radiation was partially blocked by the sides of our microcosms, reducing radiation by an average of 50% depending on solar angle. Litter cover at Sevilleta NWR, New Mexico averages about 25% [*Ryerson and Parmenter*, 2001]. Thus, after accounting for litter cover, we estimate that litter mass lost photochemically as CO_2 in a heterogeneous landscape would realistically be about 1 g C m^{-2} a^{-1}.

[34] To compare mass lost over 1 year via photodegradation to total litter mass lost over 1 year of decomposition in arid ecosystems, we used a simple exponential decay model: $X = X_0 e^{-kt}$, where k is the intrinsic rate of decay, t is time in years, X_0 is the initial litter mass, and X is the litter mass remaining at time t [*Olson*, 1963]. Aboveground net primary production (ANPP) in desert grasslands in New

Figure 9. Cumulative C respired over a 21-day period per microcosm from soil amended with litter that had been either sterilized or not sterilized prior to being buried in soil. There was no significant difference between pre-irradiated and unirradiated litter, and these two treatments were pooled. Means (n = 14) and standard error shown. Letters indicate significant pair-wise differences (Tukey's HSD). See Table 1 for species codes.

Mexico is 20 g litter m^{-2} a^{-1} during dry years [*Muldavin et al.*, 2008] and is a realistic estimate for litter production as grassland ANPP turns over each year. Previous studies have estimated exponential decay rates (k) of decomposing litter in arid systems in dry years at 0.2 g g^{-1} a^{-1} [*Yahdjian et al.*, 2006; *Brandt et al.*, 2007]. Substituting 20 for X_0, 0.2 for k, and 1 for t, we expect a mass loss of approximately 4 g litter m^{-2} over the first year of decomposition. Therefore, litter mass lost as CO_2 via photodegradation (estimated as 1 g C m^{-2} a^{-1} above) would account for approximately 25% of litter mass loss when litter productivity is low and solar irradiance is high.

[35] On the basis of our estimates, CO_2 fluxes from photodegrading plant litter are greater than carbon monoxide (CO) fluxes. Although we did not measure CO in this study, we can estimate fluxes on the basis of published relationships between CO fluxes and solar irradiance. *Schade et al.* [1999] estimated a CO flux from dry plant matter of 3.7×10^{12} molecules J^{-1} for broadleaves and 5.8×10^{11} molecules J^{-1} for grasses, which is equivalent to 0.074 and 0.012 μg C kJ^{-1}, respectively. These fluxes are approximately 7% of our observed CO_2 fluxes. Therefore, while CO does contribute to C losses from photodegradation, the primary mechanism for C loss from plant litter appears to be as CO_2. *Miller and Zepp* [1995] observed a similar contrast between DIC and CO fluxes in the ocean, where DIC fluxes were 20 times higher than those of CO.

[36] Using ambient solar radiation, we found that PAR wavelengths are almost equally as important as UV wavelengths in photochemical CO_2 production. UV-B, UV-A, and PAR in the 400–500 nm range contributed 37%, 18%, and 45% of total CO_2 production, respectively. Using UV lamps in the lab, *Anesio et al.* [1999a] found that UV-A wavelengths were more important than UV-B, but they did not investigate the importance of PAR. Previous field studies examining litter mass loss have only manipulated a subset of UV-B, UV-A + B or PAR [*Pancotto et al.*, 2003, 2005; *Austin and Vivanco*, 2006; *Gallo et al.*, 2006; *Brandt et al.*, 2007; *Day et al.*, 2007]. Therefore, it has been difficult to determine whether differences in results among studies arose from differences in site or litter characteristics or owing to the wavelengths being manipulated. Indeed, smaller positive effects on litter decomposition were observed in studies that only manipulated UV-B radiation [*Pancotto et al.*, 2005; *Day et al.*, 2007] or total UV [*Gallo et al.*, 2006; *Brandt et al.*, 2007], compared to a study that manipulated total solar radiation [*Austin and Vivanco*, 2006]. Therefore, any interpretation of the relative importance of photodegradation in different ecosystems or different litter types on the basis of different experiments should consider the wavelengths being manipulated.

[37] Contrary to our expectations, photochemically induced CO_2 production from plant litter did not differ among litter species when standardized for surface area, despite a large contrast in lignin concentration. While ecological literature has indicated lignin as the primary plant material susceptible to photodegradation by UV radiation [*Moorhead and Callaghan*, 1994], photochemical production of CO_2 and other gaseous photoproducts (including CO and CH_4) from cellulose was documented as early as the 1960s [*Desai and Shields*, 1969]. These results suggest that differences observed in the relative amount of photodegradation among different plant litters depend on factors other than the lignin concentration of the litter. One possible explanation for different effects of photodegradation for different litters observed in field studies may be differences in leaf morphology among species [*Gallo*, 2006]. Since photochemically derived CO_2 flux rates depend on surface area

exposed, specific leaf area (leaf area per unit mass) could be a primary control on the relative importance of photodegradation in litter of different species.

[38] We found that photochemically induced CO_2 flux rates do not decrease with length of exposure to solar radiation, at least on the time scales observed in this study (10 weeks). In contrast, DIC production rates in aquatic systems decrease with increasing exposure [*Miller and Zepp*, 1995]. If the pattern of constant CO_2 production rate holds over longer time periods (i.e., years), this could explain why litter decomposition in arid ecosystems appears to follow a linear pattern of decay instead of an exponential or asymptotic decay model observed in more mesic environments [*Adair et al.*, 2008]. Since photochemical degradation depends on litter surface area, while biological degradation depends on litter mass, the differences in these patterns are as expected. With biological decomposition, decay follows first-order kinetics (i.e., the rate is proportional to the amount of mass remaining). In contrast, a reaction that only happens on the surface would be expected to follow a pseudo zero-order decay (i.e., the rate is independent of mass) as long as surface area remains constant. This pattern of decomposition has important implications for how we approach large-scale estimates of decomposition rates.

5. Conclusions

[39] Our results suggest that photochemical mineralization to CO_2 is the primary mechanism by which C is lost from litter during photodegradation, as opposed to leaching, other direct gaseous losses, or biological facilitation. Further, we show that both UV and PAR wavelengths are important for this mechanism. Direct abiotic mineralization to CO_2 via photodegradation should be considered as a major mechanism for litter turnover in systems with high levels of solar radiation, low litter inputs, and low levels of microbial activity. This process is therefore important as a mechanism for C loss from decomposing plant litter in arid ecosystems. As arid ecosystems represent one of the largest land cover types in the world, a greater understanding of the role of photochemical CO_2 production at regional and global scales is essential. Further empirical and modeling work is needed in order to elucidate the importance of photochemical CO_2 production in litter decomposition dynamics and the global carbon cycle.

[40] **Acknowledgments.** We thank S. Graves, K. Crooker, Y. Sorokin, K. Hill, F. Walosin, and M. Stursova for their assistance in litter collection and sample preparation. We thank S. Hobbie and R. Cory for their assistance in the experimental design and for their helpful comments on the manuscript. We appreciate helpful suggestions from two anonymous reviewers and from the editors. This project was funded by NSF DEB-0542935, an EPA STAR Fellowship to L. Brandt, a doctoral dissertation improvement grant to L. Brandt, and an REU supplement to support participation of REU student C. Bohnet.

References

Adair, E. C., W. J. Parton, S. J. Del Grosso, W. L. Silver, M. E. Harmon, S. A. Hall, I. C. Burke, and S. C. Hart (2008), Simple three-pool model accurately describes patterns of long-term litter decomposition in diverse climates, *Global Change Biol.*, *14*, 1–25, doi:10.1111/j.1365-2486.2008.01674.x.

Amado, A. M., J. B. Cotner, A. L. Suhett, F. de Assis Esteves, R. L. Bozelli, and V. F. Farjalla (2007), Contrasting interactions mediate dissolved organic matter decomposition in tropical aquatic ecosystems, *Aquat. Microbiol. Ecol.*, *49*(1), 25–34, doi:10.3354/ame01131.

Amon, R. M. W., and R. Benner (1996), Photochemical and microbial consumption of dissolved organic carbon and dissolved oxygen in the Amazon River system, *Geochim. Cosmochim. Acta*, *60*(10), 1783–1792, doi:10.1016/0016-7037(96)00055-5.

Anesio, A. M., L. J. Tranvik, and W. Granéli (1999a), Production of inorganic carbon from aquatic macrophytes by solar radiation, *Ecology*, *80*(6), 1852–1859.

Anesio, A. M., C. M. T. Denward, and L. J. Tranvik (1999b), Decreased bacteria growth on vascular plant detritus due to photochemical modification, *Aquat. Microbiol. Ecol.*, *17*(2), 159–165, doi:10.3354/ame017159.

Austin, A. T., and L. Vivanco (2006), Plant litter decomposition in a semiarid ecosystem controlled by photodegradation, *Nature*, *442*(7102), 555–558, doi:0.1038/nature05038.

Austin, A. T., L. Yahdjian, J. M. Stark, J. Belnap, A. Porporato, U. Norton, D. A. Ravetta, and S. M. Schaeffer (2004), Water pulses and biogeochemical cycles in arid and semiarid ecosystems, *Oecologia*, *141*(2), 221–235, doi:10.1007/s00442-004-1519-1.

Belnap, J., S. L. Phillips, S. Flint, J. Money, and M. Caldwell (2008), Global change and biological soil crusts: Effects of ultraviolet augmentation under altered precipitation regimes and nitrogen additions, *Global Change Biol.*, *14*(3), 670–686, doi:10.1111/j.1365-2486.2007.01509.x.

Brandt, L. A., J. Y. King, and D. G. Milchunas (2007), Effects of ultraviolet radiation on litter decomposition depend on precipitation and litter chemistry in a shortgrass steppe ecosystem, *Global Change Biol.*, *13*(10), 2193–2205, doi:0.1111/j.1365-2486.2007.01428.x.

Day, T. A., E. T. Zhang, and C. T. Ruhland (2007), Exposure to solar UV-B radiation accelerates mass and lignin loss of *Larrea tridentata* litter in the Sonoran Desert, *Plant Ecol.*, *193*(2), 185–194, doi:10.1007/s11258-006-9257-6.

Deichmann, U., and L. Eklundh (1991), Global digital data sets for land degradation studies: A GIS approach, *GRID Case Study Ser. 4*, U. N. Environ. Prog. Global Resour. Info. Database, Nairobi, Kenya.

Desai, R. L., and J. A. Shields (1969), Photochemical degradation of cellulose material, *Makromol. Chem.*, *122*, 134–144, doi:10.1002/macp.1969.021220111.

Gallo, M. E. (2006), Photodegradation and plant litter decomposition in arid ecosystems, Ph.D. thesis, 101 pp., Univ. of N. M., Albuquerque, N. M.

Gallo, M. E., R. L. Sinsabaugh, and S. E. Cabaniss (2006), The role of ultraviolet radiation in litter decomposition in arid ecosystems, *Appl. Soil Ecol.*, *34*(1), 82–91, doi:10.1016/j.apsoil.2005.12.006.

Gehrke, C., U. Johanson, T. V. Callaghan, D. Chadwick, and C. H. Robinson (1995), The impact of enhanced ultraviolet-B radiation on litter quality and decomposition processes in *Vaccinium* leaves from the subarctic, *Oikos*, *72*(2), 213–222, doi:10.2307/3546223.

Gholz, H. L., D. A. Wedin, S. M. Smitherman, M. E. Harmon, and W. J. Parton (2000), Long-term dynamics of pine and hardwood litter in contrasting environments: Toward a global model of decomposition, *Global Change Biol.*, *6*(7), 751–765, doi:10.1046/j.1365-2486.2000.00349.x.

Granéli, W., M. Lindell, B. Marçal de Faria, and F. de Assis Esteves (1998), Photoproduction of dissolved inorganic carbon in temperate and tropical lakes-dependence on wavelength band and dissolved organic carbon concentration, *Biogeochemistry*, *43*(2), 175–195, doi:10.1023/A:1006042629565.

Kemmitt, S. J., C. V. Lanyon, I. S. Waite, Q. Wen, T. M. Addiscott, N. R. A. Bird, A. G. O'Donnell, and P. C. Brookes (2008), Mineralization of native soil organic matter is not regulated by the size or composition of the soil microbial biomass-a new perspective, *Soil Biol. Biochem.*, *40*(1), 61–73, doi:10.1016/j.soilbio.2007.06.021.

Miller, W. L., and R. G. Zepp (1995), Photochemical production of dissolved inorganic carbon from terrestrial organic matter: Significance to the ocean carbon cycle, *Geophys. Res. Lett.*, *22*(4), 417–420, doi:10.1029/94GL03344.

Moore, D. (2003), Sevilleta Long Term Ecological Research Meteorological Data Set, Site Database SEV001, Univ. of N. M., Albuquerque, N. M. (Available at http://sev.lternet.edu/dataget.php?id=16)

Moorhead, D. L., and T. Callaghan (1994), Effects of increasing ultraviolet B radiation on decomposition and soil organic matter dynamics: A synthesis and modeling study, *Biol. Fertil. Soils*, *18*(1), 19–26, doi:10.1007/BF00336439.

Muldavin, E. H., D. I. Moore, S. L. Collins, K. R. Wetherill, and D. C. Lightfoot (2008), Aboveground net primary production dynamics in a northern Chihuahuan Desert ecosystem, *Oecologia*, *155*(1), 123–132, doi:10.1007/s00442-007-0880-2.

Olson, J. S. (1963), Energy storage and the balance of producers and decomposers in ecological systems, *Ecology*, *44*(2), 322–331, doi:10.2307/1932179.

Pancotto, V. A., O. E. Sala, M. Cabello, N. Lopez, T. M. Robson, C. L. Ballare, M. M. Caldwell, and A. L. Scopel (2003), Solar UV-B decreases decomposition in herbaceous plant litter in Tierra del Fuego, Argentina:

Potential role of an altered decomposer community, *Global Change Biol.*, *9*(10), 1465–1474, doi:10.1046/j.1365-2486.2003.00667.x.

Pancotto, V. A., O. E. Sala, T. M. Robson, C. L. Ballare, M. M. Caldwell, and A. L. Scopel (2005), Direct and indirect effects of solar ultraviolet-B radiation on long-term decomposition, *Global Change Biol.*, *11*(11), 1982–1989, doi:10.1111/j.1365-2486.2005.01027.x.

Parton, W. J., W. L. Silver, I. C. Burke, L. Grassens, M. E. Harmon, W. Currie, J. Y. King, E. C. Adair, L. A. Brandt, and B. Fasth (2007), Striking global-scale similarities in nitrogen release patterns during long term decomposition, *Science*, *315*(5810), 361–364, doi:10.1126/science.1134853.

Rozema, J., M. Tosserams, H. J. M. Nelissen, L. van Heerwaarden, R. A. Broekman, and N. Flierman (1997), Stratospheric ozone reduction and ecosystem processes: Enhanced UV-B radiation affects chemical quality and decomposition of leaves of the dune grassland species *Calamagrostis epigeios*, *Plant Ecol.*, *128*(1–2), 284–294.

Ryerson, D. E., and R. R. Parmenter (2001), Vegetation change following removal of keystone herbivores from desert grasslands in New Mexico, *J. Veg. Sci.*, *12*(2), 167–180, doi:10.2307/3236602.

Schade, G. W., R. M. Hofmann, and P. J. Crutzen (1999), CO emissions from degrading plant litter: 1. Measurements, *Tellus, Ser. B*, *51*(5), 889–908, doi:10.1034/j.1600-0889.1999.t01-4-00003.x.

Sponseller, R. A. (2007), Precipitation pulses and soil CO_2 flux in a Sonoran Desert ecosystem, *Global Change Biol.*, *13*(2), 426–436, doi:10.1111/j.1365-2486.2006.01307.x.

Tarr, M. A., W. L. Miller, and R. G. Zepp (1995), Direct carbon monoxide photoproduction from plant matter, *J. Geophys. Res.*, *100*(D6), 11,403–11,413.

Throop, H. L., and S. R. Archer (2007), Interrelationships among shrub encroachment, land management, and litter decomposition in a semidesert grassland, *Ecol. Appl.*, *17*(6), 1809–1823, doi:10.1890/06-0889.1.

Tranvik, L. J., and S. Bertilsson (2001), Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth, *Ecol. Lett.*, *4*(5), 458–463, doi:10.1046/j.1461-0248.2001.00245.x.

Vähätalo, A., M. Søndergaard, L. Schlüter, and S. Markager (1998), Impact of solar radiation on the decomposition of detrital leaves of eelgrass *Zostera marina*, *Mar. Ecol. Prog. Ser.*, *170*, 107–117, doi:10.3354/meps170107.

Valentine, R. L., and R. G. Zepp (1993), Formation of carbon monoxide from the photodegradation of terrestrial dissolved organic carbon in natural waters, *Environ. Sci. Technol.*, *27*(2), 409–412, doi:10.1021/es00039a023.

Van Soest, P. J. (1967), Development of a comprehensive system of feed analysis and its application to forages, *J. Animal Sci.*, *26*, 119–128.

Vigano, I., H. van Weelden, R. Holzinger, F. Keppler, and T. Röckmann (2008), Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components, *Biogeosci. Discuss.*, *5*, 243–270.

Vossbrinck, C. R., D. C. Coleman, and T. A. Woolley (1979), Abiotic and biotic factors in litter decomposition in a semiarid grassland, *Ecology*, *60*(2), 265–271, doi:10.2307/1937654.

Wetzel, R. G., P. G. Hatcher, and T. S. Bianchi (1995), Natural photolysis by ultraviolet irradiance of recalcitrant dissolved organic matter to simple substrates for rapid bacterial metabolism, *Limnol. Oceanogr.*, *40*(8), 1369–1380.

Yahdjian, L., O. Sala, and A. Austin (2006), Differential controls of water input on litter decomposition and nitrogen dynamics in the Patagonian steppe, *Ecosystems*, *9*(1), 128–141, doi:10.1007/s10021-004-0118-7.

C. Bohnet, Department of Biology, University of Northern Iowa, 144 McCollum Science Hall, Cedar Falls, IA 50614, USA.

L. A. Brandt, Department of Ecology, Evolution and Behavior, University of Minnesota, 1987 Upper Buford Circle, St. Paul, MN 55108, USA. (brand142@umn.edu)

J. Y. King, Department of Geography, University of California, Santa Barbara, CA 93106, USA. (jyking@geog.ucsb.edu)