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# Thermal abiotic emission of CO<sub>2</sub> and CH<sub>4</sub> from leaf litter and its significance in a photodegradation assessment

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**Abstract.** Photodegradation has been recognized as a significant driver of plant litter decomposition in drylands. Another potential driver is the thermal emission of trace gases that occurs in the absence of solar radiation and microbial activity. Most field assessments documenting photodegradation have employed filters that absorb solar radiation, along with transparent filter controls; faster litter decay under transparent filters is taken as evidence of photodegradation. However, the temperature of litter under transparent filters is often higher, and its faster decay might conceivably stem from greater thermal emission, rather than photodegradation. If true, the growing consensus that photodegradation is a significant driver of litter decay needs rethinking. We assessed the contribution of thermal emission of CO<sub>2</sub> and CH<sub>4</sub> to the C loss of 12 litter types over a 34-month photodegradation study in the Sonoran Desert by quantifying thermal emission responses and using field litter temperatures to estimate emissions. Emission of both gases from litter increased exponentially with temperature. Emission of CO<sub>2</sub> was much greater than CH<sub>4</sub>, but their rates were strongly correlated. Concentrations of surface waxes and dissolved organic C in litter were strong predictors of emission of both gases. Emission declined from dried green leaves to naturally senesced litter, and as litter decayed. Diurnal litter temperature averaged 39.8°C under transparent filters over the field experiment and averaged 1.7°C higher than that of litter under filters that absorbed UV through blue solar wavelengths. Through all mechanisms, litter lost an average of 77.8% of its original C under transparent filters and 60.8% under filters that absorbed UV through blue wavelengths. However, thermal emission of these gases accounted for only 0.8% of the original C in litter under transparent filters and 1.0% under filters that absorbed UV through blue wavelengths, corresponding to only 1.2% and 2.0% of the total C lost from litter. While litter temperatures were higher under transparent filters, thermal emission losses from this litter were lower because emission from this litter declined faster with decay. We conclude that thermal abiotic emission was a minor C loss pathway and that photodegradation was responsible for the faster decay of litter in sunlight.

**Key words:** carbon dioxide; drylands; litter decomposition; methane; photodecay; photodegradation; Sonoran Desert; temperature; thermal degradation; thermal emission; wax.

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## INTRODUCTION

Decomposition of plant litter represents a substantial pathway for C flux from land to the atmosphere, but our understanding of the mechanisms driving this process is particularly limited

in drylands. For example, differences in decay rates among litter types are usually well predicted by indices of litter decomposability by microbes (which we hereafter refer to as litter quality), such as C:N or lignin:N ratios (Meentemeyer 1978, Melillo et al. 1982, Cornwell et al.

2008). A notable exception is drylands, where these indices fail to predict differences in decay among litter types (Schaefer et al. 1985, Cepeda-Pizarro and Whitford 1990, Vanderbilt et al. 2008, Day et al. 2018, Liu et al. 2018). In many terrestrial ecosystems, decay rates are well predicted by models that incorporate these litter-quality indices together with climatic indices that estimate microbial activity. A notable exception is drylands, where these models consistently underestimate decay (Adair et al. 2008).

These shortcomings have led to suggestions that additional drivers of litter decay are at work in drylands. One such driver is photodegradation, which we define as the decay of litter by exposure to solar radiation caused by abiotic photolysis, along with any subsequent effects this may have in accelerating decay, such as through faster degradation by microbes. Abiotic photolysis involves both direct photolysis (fragmentation of a compound that absorbs radiation) and indirect photolysis (fragmentation of a compound caused by energy transfer from an adjacent compound that absorbs radiation; King et al. 2012). Along with photolysis, exposure to solar radiation can also make litter more amenable to microbes, accelerating microbial degradation of this litter, a process referred to as photoprimering (Foereid et al. 2010, Frouz et al. 2011, Baker and Allison 2015, Barnes et al. 2015, Austin et al. 2016, Day et al. 2018, Lin et al. 2018). Over the past decade, several field studies have demonstrated that exposure to solar radiation accelerates the decay of terrestrial plant litter (reviewed by King et al. 2012, Barnes et al. 2015, Wang et al. 2015). Most of these studies have been conducted in drylands where high solar irradiance and low moisture availability are perceived to favor photodegradation over other mechanisms such as degradation by microbes or leaching. In a meta-analysis, King et al. (2012) found that exposure to solar UV radiation (280–400 nm), or all solar radiation, increased litter mass loss on average by 1.3 and 1.6 times, respectively. Hence, photodegradation can be significant and provides one explanation for the faster than expected litter decay in drylands. Furthermore, the inclusion of photodegradation in decomposition models improves their ability to predict litter mass and C losses (Chen et al. 2016, Adair et al. 2017), as well as N cycling (Asao et al. 2018), in drylands. There is growing

evidence that the contribution of photoprimering, through promoting microbial degradation, may overshadow that of abiotic photolysis, in terms of accelerating mass or C loss under photodegradation (Wang et al. 2015, Austin et al. 2016, Gliksmann et al. 2017, Day et al. 2018, Lin et al. 2018). Nevertheless, abiotic photolysis is well documented. For example, exposure to solar or UV radiation can accelerate abiotic trace-gas emission from litter, which we refer to as photochemical emission. This includes photochemical emission of CO<sub>2</sub> (Brandt et al. 2009, Rutledge et al. 2010, Lee et al. 2012), CH<sub>4</sub> (Keppler et al. 2006, Vigano et al. 2008, 2009, Bruhn et al. 2009, Lee et al. 2012), and CO (Tarr et al. 1995, Schade et al. 1999, Lee et al. 2012).

Notably, emission of these trace gases from litter or dried leaves has also been documented in the absence of solar radiation and microbial activity. We refer to this abiotic temperature-induced emission of trace gases, in the absence of solar radiation and microbial activity, as thermal emission. These emissions are typically very low at temperatures below 30°C, but increase exponentially at higher temperatures, particularly above ≈50°C (but well below the ignition point of organic matter). While this process is not well characterized (reviewed by Carmichael et al. 2014, Wang et al. 2017), Lee et al. (2012) found that thermal emission of CO<sub>2</sub> and CH<sub>4</sub> from dried green leaves of four species, as well as cellulosic filter paper and basswood wood, increased exponentially from 25°C to 55°C. Rates varied appreciably among plant materials implying that chemical composition is a potential factor in emission rates. They suggested that multiple mechanisms and compounds may be involved, including the breaking of carboxyl and carbonyl groups, and that lignin may be an emission source based on the higher emission from higher-lignin material (i.e., wood). Keppler et al. (2006) and Vigano et al. (2008) also found that thermal emission of CH<sub>4</sub> from dried leaves of several species increased with temperature. Keppler et al. (2006) suggested that pectins, a component of cell walls, are one likely source. Hurkuck et al. (2012) found that thermal emission of CH<sub>4</sub> from lignin and pectin both increased exponentially from 30°C to 70°C, with the emission rate from lignin being roughly twice that from pectin at 70°C. Several others have documented

photochemical  $\text{CH}_4$  emission from pectins (McLeod et al. 2008, Vigano et al. 2008, Bruhn et al. 2009, Messenger et al. 2009), as well as from lignin and cellulose (Vigano et al. 2008). More recently, Bruhn et al. (2014) found appreciable photochemical  $\text{CH}_4$  emission from leaf surface waxes. Lee et al. (2012) suggested that some of the photochemical emission of  $\text{CH}_4$  was instantaneously oxidized to  $\text{CO}_2$  or  $\text{CO}$ , based on the higher emission rates of  $\text{CH}_4$  they observed in the absence of  $\text{O}_2$ . Thermal emission of another trace gas,  $\text{CO}$ , has also been documented from dried (Lee et al. 2012) and live (Bruhn et al. 2013) leaves, as well as senescent plant material (Schade et al. 1999), and also increases exponentially with temperature. Tarr et al. (1995) found photochemical emission of  $\text{CO}$  was greatest from naturally abscised leaves (i.e., brown litter), intermediate from attached leaves in various stages of senescence (i.e., still retaining some photosynthetic pigments), and lowest from attached living (green) leaves, and Bruhn et al. (2013) found greater emission from dried green than live leaves, illustrating that abiotic emission, at least photochemical emission, can vary by leaf physiological status and litter age.

Failing to account for thermal emission could conceivably lead to disconcerting overestimates of litter photodegradation in drylands. For example, most field experiments examining litter photodegradation have entailed placing optical filters that absorb wavebands of solar radiation (usually UV and sometimes lower visible wavebands; i.e., violet and blue), above litter. When litter under transparent filters decays faster, the faster decay has been attributed to photodegradation (or subsequent synergistic effects attributable to photoprimering such as enhanced microbial degradation). However, the greater solar irradiance of litter under transparent filters invariably leads to higher litter temperatures. Hence, the faster decay of this litter might be attributable to greater thermal emission rather than photodegradation per se. As such, van Asperen et al. (2015) suggested that studies assessing photodegradation may have overestimated the role of photodegradation and that the greater trace-gas emission or mass loss from litter under greater solar irradiance might be entirely the result of accelerated thermal emission associated with higher temperatures. If true, the

growing consensus that photodegradation is a significant driver of litter decay is invalid, and attempts to refine models of litter decay and nutrient cycling by including a photodegradation component will be flawed. To our knowledge, the potential significance of thermal emission to litter decay or its relevance in photodegradation assessments has not been explicitly tested.

The Sonoran Desert in central Arizona provides an ideal setting to assess thermal emission, as well as test its significance in a photodegradation assessment. Daily diurnal temperatures of sunlit litter on the soil surface often average  $>50^\circ\text{C}$  during the summer, with temperatures occasionally exceeding  $80^\circ\text{C}$  (Day et al. 2018). Furthermore, high solar irradiance promotes higher litter temperatures in photodegradation treatments that receive more solar radiation, which should favor higher thermal emission in these treatments. In a recent study, we identified what litter traits predicted the litter mass loss of 12 leaf litter types and assessed how exposure to solar radiation influenced mass loss over 34 months in the Sonoran Desert (Day et al. 2018). In brief, we found that litter microbial respiration rates were the strongest predictor of litter mass loss. We also found that litter exposed to full sunlight lost on average 1.5 times more mass than litter filtered from UV through blue solar wavelengths, implying that photodegradation is a significant driver of litter decay, consistent with past studies at this site (Day et al. 2007, 2015). As expected, diurnal temperatures of litter exposed to full sunlight were consistently, and often appreciably, higher than those of litter filtered from UV through blue wavelengths, although we did not address the potential implications of these higher temperatures.

In this study, we quantified the thermal response of emission of  $\text{CO}_2$  and  $\text{CH}_4$  from the 12 litter types in the laboratory and used field litter temperature to assess the significance of thermal emission to litter C loss over the field experiment. Our main objectives were to (1) assess the contribution of thermal emission of  $\text{CO}_2$  and  $\text{CH}_4$  to litter C loss over the field experiment and (2) evaluate whether presumably greater emission from litter in full sunlight (caused by higher temperatures) could explain the greater C loss of this litter. We also characterized how emission changed as litter decayed in

the field, and whether it differed between litter exposed to full sunlight or filtered from UV through blue wavelength radiation, and accounted for these factors in our estimates. We also assessed what litter traits were correlated with emission rates to provide clues as to precursors of emission. Lastly, we measured emission from isolated compounds that we found to be strong predictors of emission (waxes and water-soluble fractions) or that others have suggested to be precursors (pectin, cellulose, and hemicellulose), to assess their relative potential as precursors of emission.

## METHODS

### *Field experiment: litter collection, field site, radiation treatments, and litter decay*

We assessed the thermal emission response of leaf litter in the laboratory in conjunction with a parallel field experiment in which we assessed the influence of sunlight exposure on the mass loss of 12 leaf litter types in the Sonoran Desert in Phoenix, Arizona, USA, described by Day et al. (2018). For both the thermal emission measurements and the field experiment, we used litter that we collected from May through July 2013 in the Sonoran Desert of central Arizona. Litter was collected as naturally senesced leaves (i.e., lacking photosynthetic pigments) that were attached to standing branches/stems from several individuals of 12 plant species. We hereafter refer to this material as initial litter and distinguish it from live green leaves that we also collected and dried and refer to as dried green leaves. The 12 species or litter types consisted of four species of three different growth forms: woody dicots (*Simmondsia chinensis*, *Olneya tesota*, *Prosopis velutina*, *Larrea tridentata*), suffrutescent dicots (*Ambrosia deltoidea*, *Baileya multiradiata*, *Encelia farinosa*, *Encelia frutescens*), and grasses (*Aristida purpurea*, *Bromus rubens*, *Cynodon dactylon*, *Eragrostis curvula*) (see Appendix S1: Table S1). Litter was air-dried (22°C at 10–20% relative humidity) for at least 30 d and sorted to remove non-leaf parts. We measured thermal emission of this initial litter, as well as older litter that was exposed to different wavebands of sunlight over the course of the field experiment. For the field experiment, litter was placed in envelopes (10 × 10 cm) whose tops were constructed of filter material that either (1)

transmitted all solar wavebands (i.e., transmitted >80% of solar UV and visible radiation, using Aclar Type 22A filters [Proplastics, Linden, New Jersey, USA]) which we refer to as the full sun treatment or (2) absorbed most solar UV and low-wavelength visible radiation through the blue waveband (i.e., having a sharp cutoff with 50% transmittance at 545 nm, using Amber UV filters [UVPS, Chicago, Illinois, USA]) which we refer to as the No UV/blue treatment. Envelope bottoms were 153-μm mesh screening (Nitex cloth; Wildlife Supply, Buffalo, New York, USA). Each envelope received 0.88–2.39 g (±0.05 g) of air-dried litter, depending on litter type, which corresponded to a total litter surface area of ≈80% of the surface area of the envelope. Envelopes were deployed in a randomized block design involving 12 litter types × 2 radiation treatments × 7 collection times × 8 replicates and placed in eight blocks or plots in unshaded level areas void of shrubs for ≥1 m from plot edges, in a conservation area at the Desert Botanical Garden, Phoenix, Arizona, USA (Appendix S1: Fig. S1). Envelopes were anchored firmly to the soil surface with nails inserted through envelope corners. Litter envelopes were placed in the field on 16 December 2013. Eight replicate envelopes of each litter type/treatment combination (one from each of the eight plots) were collected after 67, 135, 196, 327, 492, 634, and 1046 d (24 October 2016) in the field and used to determine litter mass loss. We measured thermal emission from initial litter and litter collected from the two radiation treatments after 135 and 327 d in the field (30 April and 8 November 2014). Following collection, litter envelope contents were gently poured onto white paper, and extraneous material was removed. The remaining litter sample contained litter along with any soil/microbial film that adhered to its surface. The sample was oven-dried (OD, 60°C for 24 h), and a subsample was ashed (550°C for 6 h), and mass loss was calculated on an oven-dry, ash-free basis.

We monitored litter air temperatures over the field experiment in five extra envelopes of the full sun and the No UV/blue filter treatments containing *Simmondsia chinensis* litter placed on the ground surface adjacent to our main plots. A Hygrochron Temperature/Humidity Logger (DS1923, iButtonLink, Whitewater, Wisconsin, USA) was inserted underneath the litter inside each envelope so that it was shaded, and to



further minimize absorptance of solar radiation, we wrapped the top and side of each Hygrochron with white Teflon tape. Hygrochrons recorded litter air temperature every hour over the field experiment. We summarized litter temperatures by examining both diel and diurnal periods, and defined the latter as hours in which the visible irradiance averaged  $>2 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ . Visible irradiance was measured 1.5 m above the ground with a quantum sensor (LI-190SA; LICOR, Lincoln, Nebraska, USA) every minute and summarized as hourly means over the experiment with a datalogger (CR23X; Campbell Scientific, Logan, Utah, USA).

### *Litter traits*

We measured several chemical and anatomical traits of initial litter to assess what traits might predict emission rates. Five subsamples of each litter type ( $1.2 \pm 0.1$  g air-dried) were oven-dried and combusted in a muffle furnace to measure ash (i.e., inorganic) concentration. We measured the one-sided silhouette surface area of another set of subsamples (20 pieces of each litter type) with a digital scanner and oven-dried this litter to calculate specific leaf area (SLA,  $\text{g}/\text{cm}^2$ ). Another five subsamples of each litter type were finely ground in a ball mill, and samples ( $2.5 \pm 0.2$  mg air-dried) were analyzed for organic C and N concentrations with a flash combustion elemental analyzer (PE2400; PerkinElmer, Waltham, Massachusetts, USA). Another five subsamples were ground in a Wiley mill (1-mm screen) and samples ( $0.50 \pm 0.05$  g air-dried) were analyzed for C fractions (cellulose, hemicellulose, lignin) with sequential digestion using an ANKOM fiber analyzer (ANKOM Technology, Macedon, New York, USA), as described in Day et al. (2018). We also assessed the water-soluble fraction of litter, which we define as the component removed during heating/stirring in water for 1 h. Five subsamples ( $0.05 \pm 0.01$  g air-dried) of each litter type were oven-dried, weighed, placed in 5 mL of nanopure water in 25-mL Erlenmeyer flasks, and heated and gently stirred at  $50^\circ\text{C}$  on a hotplate/stirrer. After 1 h, flask contents were filtered through  $10\text{-}\mu\text{m}$  polyethylene mesh and litter material recovered from the mesh was oven-dried and ashed. The water-soluble fraction that was extracted was expressed as a percentage of the original oven-dried organic

mass. We also measured the concentration of dissolved organic C (DOC) in the water-soluble extracts. Extracts were filtered through  $0.2\text{-}\mu\text{m}$  polycarbonate mesh, and a 2-mL subsample was diluted with nanopure water using a 1:10 ratio and analyzed for DOC with a TOC/N Analyzer (Shimadzu TOC-V/TN, Columbia, Maryland, USA). A standard curve was developed with potassium hydrogen phthalate, and DOC concentrations were corrected for dilution. We also assessed surface wax concentrations following McWhorter (1993). Four subsamples, each containing  $24 \pm 10 \text{ cm}^2$  one-sided silhouette surface area, were oven-dried, weighed, and gently stirred for 30 s in 10 mL of chloroform (CAS: 67-66-3; VWR, Radnor, Pennsylvania, USA) in a 50-mL Erlenmeyer flask. Flask contents were passed through filter paper (filter 09-801C; Fisher Scientific, Hampton, New Hampshire, USA), that was prewashed with chloroform, into preweighed 20-mL scintillation vials. To ensure all wax was removed from flasks, they were rinsed with an additional 5 mL of chloroform which was also filtered into the vials. Vial contents were dried under a stream of air at room temperature and reweighed. Concentrations were calculated on both a dry-mass ( $\text{mg}/\text{g}$ ) and one-sided silhouette surface-area basis ( $\text{mg}/\text{cm}^2$ ) and used for correlation analyses with emission rates.

### *Emission rates and thermal response*

Four replicate subsamples ( $0.20 \pm 0.05$  g air-dried) of each litter type/age/solar radiation treatment combination were placed in 37-mL glass serum bottles. Bottles were sealed with a septum and flushed for 5 min with dry air containing  $\approx$ ambient levels of  $\text{CO}_2$  (409 ppm),  $\text{CH}_4$  (1872 ppb), and  $\text{O}_2$  (21%, i.e., aerobic conditions). Serum bottles were incubated in the dark in a convection oven at  $37^\circ\text{C}$ ,  $44^\circ\text{C}$ ,  $55^\circ\text{C}$ , or  $70^\circ\text{C}$  for 6 h. For each run, eight empty bottles were also flushed and served as controls, and four additional bottles, each containing a Hygrochron, were used to measure relative humidity every 10 min over incubations. Hygrochron measurements confirmed that relative humidity inside serum bottles was 15–20% during all incubations. Preliminary tests at low temperature ( $22^\circ\text{C}$ ) found no detectable  $\text{CO}_2$  emission, unless we increased relative humidity  $>70\%$ , which likely activated microbial respiration, and we assumed

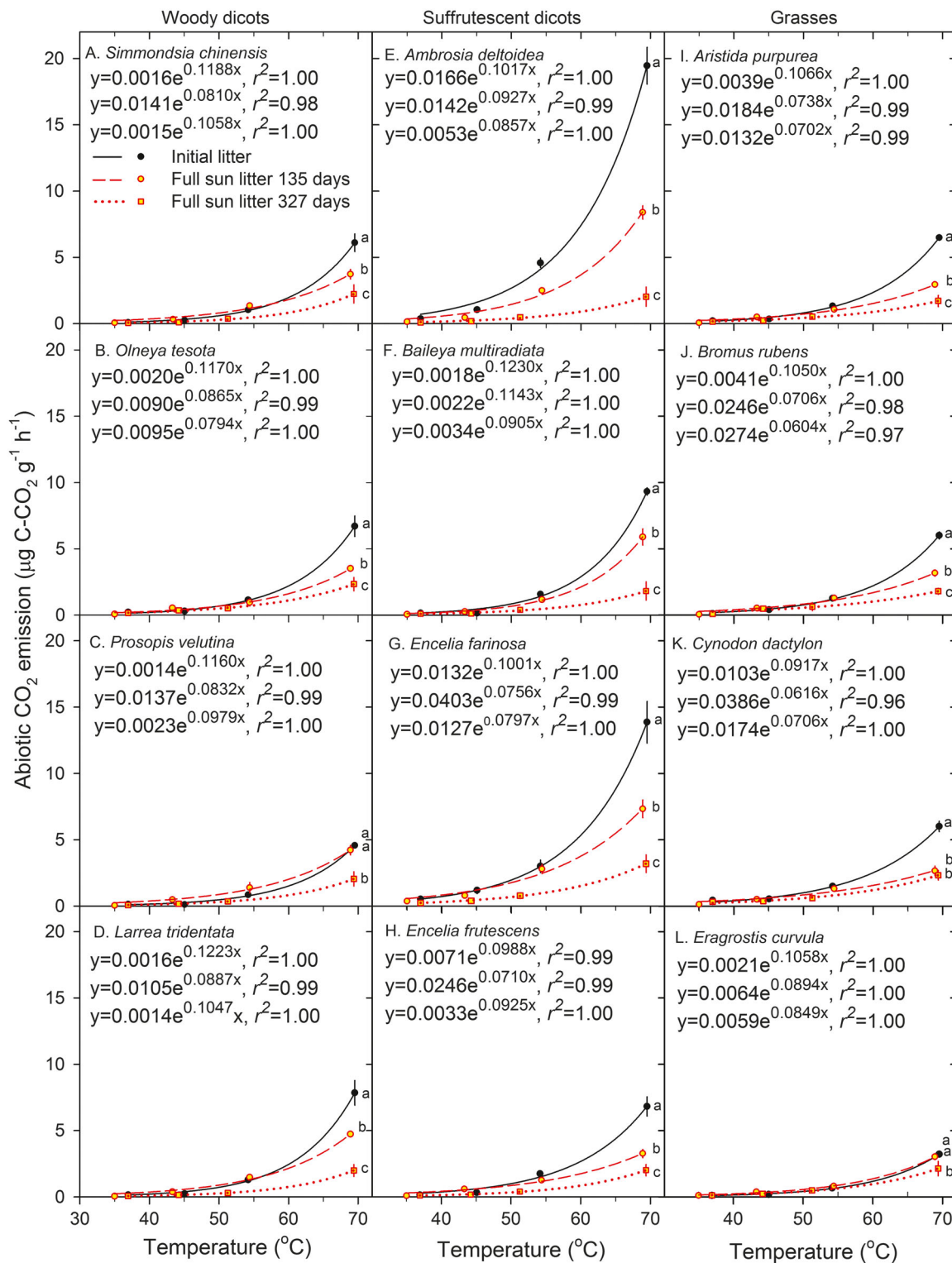


Fig. 1. Thermal response of abiotic CO<sub>2</sub> emission from initial litter and litter in the full sun treatment after 135 and 327 d in the field. Values are mean  $\pm$  standard error ( $n = 4$ ). Equations in each panel are fitted exponential

(Fig. 1. *Continued*)

regressions of initial, 135-d, and 327-d-old litter (from top to bottom, respectively). Different letters within a litter type denote significant differences in predicted emission of litter ages at 70°C ( $P \leq 0.05$ ).

that emissions in the low humidity of our incubations are abiotic and not microbial (see *Discussion*). An additional bottle contained a fine-wire thermocouple to allow real-time temperature measurement. Temperatures stabilized at their set point temperature within 10 min in the oven, after which they remained for the 6-h incubation. Temperatures varied by  $<0.7^{\circ}\text{C}$  over any given incubation period. We chose 6-h incubations, as preliminary tests found no differences in  $\text{CO}_2$  or  $\text{CH}_4$  emission rates over incubations running from 6 to 24 h (in 6-h increments). The same litter samples were used for each temperature incubation, progressing from the lowest to highest temperature. Litter was stored at  $22^{\circ}\text{C}$  and 15–20% relative humidity in the dark for at least 4 d before use in another incubation.

Immediately after flushing incubation bottles with the ambient air mix, a 1.0 mL headspace sample was drawn from four of the empty control bottles with a syringe (Hamilton Gastight SampleLock, Reno, Nevada, USA). Preliminary tests, with empty bottles as well as bottles containing litter, confirmed that our flushing protocol provided consistent initial concentrations of  $\text{CO}_2$  and  $\text{CH}_4$  among bottles. At the end of each temperature incubation, 1.0 mL samples were drawn from the bottles containing litter, along with the four remaining empty control bottles. Samples were injected into a gas chromatograph equipped with a flame-ionization detector (GC-FID, Model 310; SRI Instruments, Torrance, California, USA). Hydrogen, supplied with a  $\text{H}_2$  generator (GCCS-7890; Parker Balston, Lancaster, New York, USA), was used as a carrier gas at 7 PSI. A silica gel column, maintained at  $90^{\circ}\text{C}$ , separated  $\text{CO}_2$  from  $\text{CH}_4$ , while a methanizer converted  $\text{CO}_2$  to  $\text{CH}_4$  through  $\text{H}_2$  addition with a Ni catalyst at  $350^{\circ}\text{C}$ . Peaks were integrated with software provided with the GC. During each run, samples from three primary standards of  $\text{CO}_2$  (ranging from 200 to 1500 ppm) and  $\text{CH}_4$  (ranging from 5 to 500 ppm), along with  $\text{CO}_2$ - and  $\text{CH}_4$ -free air, were injected and provided calibration equations ( $r^2 \geq 0.99$ ). After incubation and sampling at the highest temperature, litter was oven-dried. We calculated the mass of C

emitted by converting concentrations to g C- $\text{CO}_2$  or C- $\text{CH}_4$  using the ideal gas law and expressed rates as  $\mu\text{g C-CO}_2$  or  $\text{CH}_4$  emitted  $\cdot\text{g}^{-1}$  OD litter  $\cdot\text{h}^{-1}$ . For comparisons with some past studies, we used litter SLA to convert rates from a litter dry-mass to surface-area basis.

We also measured emission from purified plant compounds that others have found to be potential emission sources. Four subsamples ( $0.25 \pm 0.01$  g air-dried) of powdered purified cellulose (CAS 9004-34-6; Sigma-Aldrich, St. Louis, Missouri, USA), pectin from citrus peel ( $\geq 74\%$  galacturonic acid, CAS 9000-69-5; Sigma-Aldrich), and xylan, a common form of hemicellulose (xylan from corn core, CAS 9014-63-5; TCI, Tokyo, Japan), were placed in serum bottles, and we assessed emission rates in 6-h incubations at  $70^{\circ}\text{C}$ . Because we found emission rates among litter types were strongly correlated with wax concentrations and water-soluble fractions (see *Results*), we also measured emission rates from these fractions that we extracted from initial litter of *Ambrosia deltoidea* and *Baileya multiradiata*. Waxes and water-soluble fractions were extracted (as previously described) from four subsamples of each litter type, and  $0.25 \pm 0.01$  g (air-dried) was placed in serum bottles and emission was measured in 6-h incubations at  $70^{\circ}\text{C}$ .

#### Statistical and data analyses

Thermal emission responses were fitted with 2-parameter exponential growth equations, while the decay of emission with litter age was fitted with 3-parameter decay equations, using SigmaPlot (V12.5; Systat Software, San Jose, California, USA). Mean comparisons of emission rates or litter traits among litter types, ages, radiation treatment, or growth forms were tested with Tukey's honestly significant difference procedure test. Correlations between emission rates and litter traits, or between emission rates of initial and old litter, or  $\text{CO}_2$  and  $\text{CH}_4$ , were tested using correlation analyses to test for significance and linear regression analyses to quantify their predictive power. The exponential increase in emission rates we observed with temperature provided linear relationships between the inverse of temperature



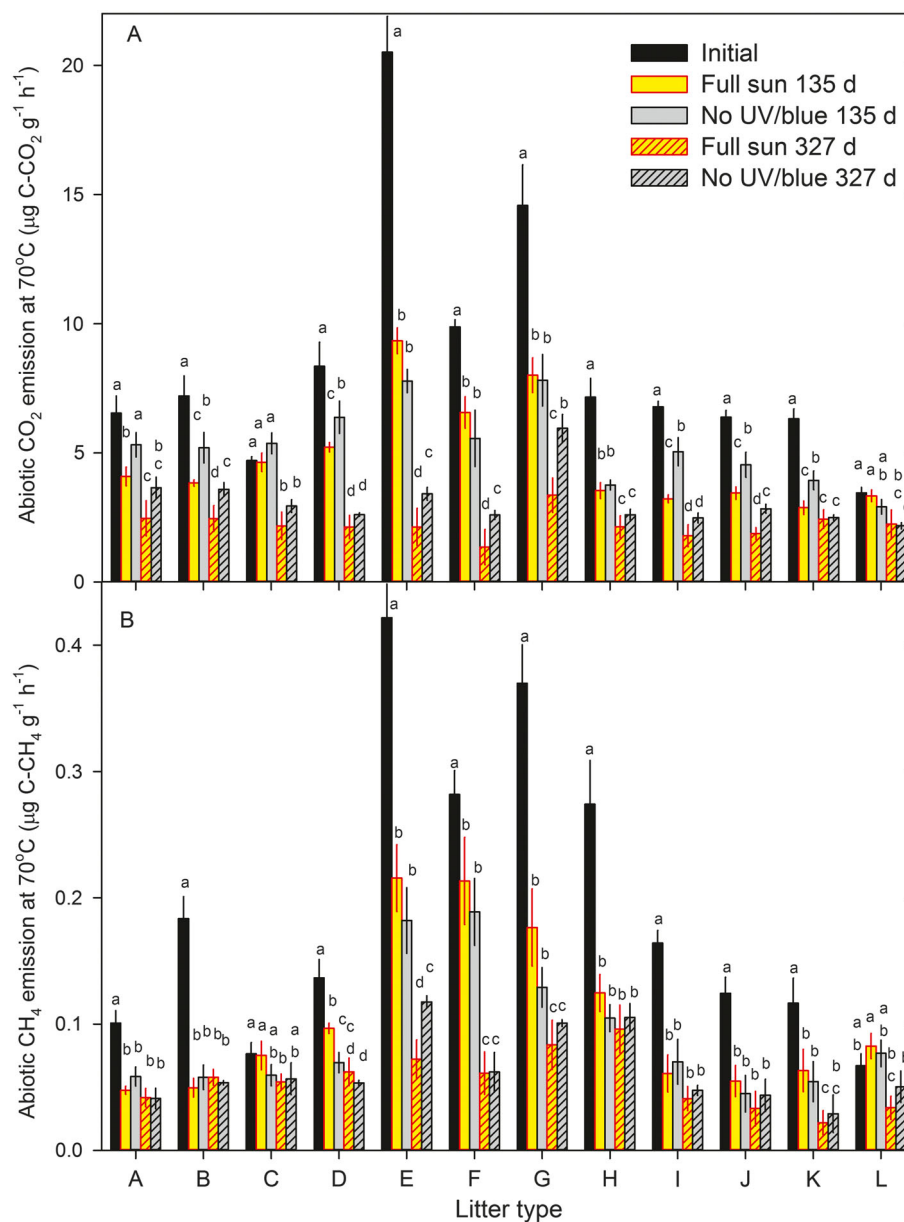


Fig. 2. Abiotic CO<sub>2</sub> (A) and CH<sub>4</sub> (B) emission at 70°C from initial litter and litter in full sun and No UV/blue treatments after 135 and 327 d in the field. Values are mean  $\pm$  standard error ( $n = 4$ ). Rates with different letters within a litter type are significantly different ( $P \leq 0.05$ ). Refer to Fig. 1 for litter type codes.

and the log of emission rates in Arrhenius plots, illustrating that the concept of activation energy was applicable. Hence, we further characterized temperature responses by calculating the activation energy ( $E_a$ ) of CO<sub>2</sub> and CH<sub>4</sub> thermal emission using the Arrhenius equation:

$$k = A \exp(-E_a/RT) \quad (1)$$

where  $k$  is the reaction rate constant,  $A$  is the pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature in Kelvins.

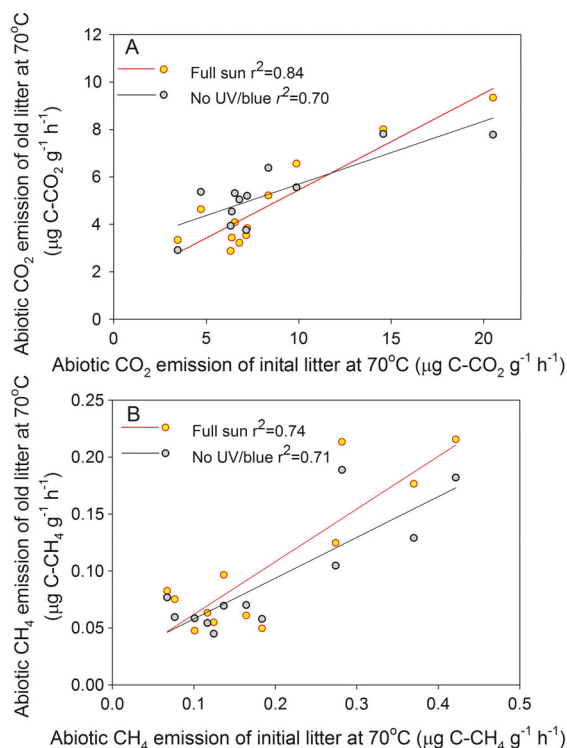


Fig. 3. Relationship between emission of CO<sub>2</sub> (A) and CH<sub>4</sub> (B) at 70°C from initial vs. old (135 d) litter. All correlations/regressions were highly significant ( $P < 0.01$ ).

## RESULTS

### Thermal response of emission

Emission of CO<sub>2</sub> from all litter types increased with temperature, and thermal responses were well described by 2-parameter exponential equations ( $r^2 \geq 0.96$ ; Fig. 1). CO<sub>2</sub> emission varied substantially among litter types, with emission at 70°C from initial litter ranging from 3.5 to 20.5  $\mu\text{g C}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ . Emission declined with litter age in nearly all litter types (Fig. 1). For example, emission (70°C) from initial litter was >135-d-old litter in full sun in 10 of 12 litter types, which was >327-d-old litter in full sun in 11 litter types. The CO<sub>2</sub> thermal responses of litter in both radiation treatments and all ages are shown in Appendix S1: Fig. S2. A similar decline in emission with age was apparent in litter in the No UV/blue treatment (Fig. 2A). The decline in CO<sub>2</sub> emission with age was generally faster in litter in the full sun treatment. For example, 135-d-old litter in full sun emitted less CO<sub>2</sub> than litter in the No

UV/blue treatment in six litter types, and 327-d-old litter in full sun emitted less CO<sub>2</sub> in five litter types (Fig. 2A). There were strong positive correlations between emission from initial litter and 135-d-old litter in both the full sun and No UV/blue treatments ( $r^2 = 0.84$  and  $0.70$ , respectively; Fig. 3A), illustrating that high initial emission of CO<sub>2</sub> was indicative of relatively high emission as this litter aged. In summary, CO<sub>2</sub> emission increased exponentially with temperature in all litter types. Emission declined as litter aged in both radiation treatments, and this decline was faster in litter in the full sun.

Emission of CH<sub>4</sub> also increased with temperature, and responses were well described by 2-parameter exponential equations ( $r^2 \geq 0.90$ , Fig. 4). Emission of CH<sub>4</sub> from initial litter also varied substantially among litter types, ranging from 0.1 to 0.7  $\mu\text{g C}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  at 70°C. The CH<sub>4</sub> thermal responses of litter in both treatments and all ages are shown in Appendix S1: Fig. S3. Emission of CH<sub>4</sub> also declined with litter age; emission (70°C) from initial litter was greater than 135-d-old litter in both radiation treatments in 10 litter types ( $P \leq 0.05$ ; Fig. 2B), which was greater than 327-d-old litter in the full sun in seven litter types, and in the No UV/blue treatment in four litter types. CH<sub>4</sub> emission from litter in the full sun and No UV/blue treatments were similar at a given age within a litter type. As was the case with CO<sub>2</sub>, there were strong positive correlations between CH<sub>4</sub> emission from initial litter and 135-d-old litter in both full sun and No UV/blue treatments ( $r^2 = 0.74$  and  $0.71$ , respectively, Fig. 3B). In summary, CH<sub>4</sub> emission increased exponentially with temperature and declined as litter aged in both radiation treatments. Unlike CO<sub>2</sub>, there were no differences in CH<sub>4</sub> emission from litter at a given age between radiation treatments.

There was a strong positive correlation between CO<sub>2</sub> and CH<sub>4</sub> emission (70°C) from initial litter ( $r^2 = 0.82$ ,  $P < 0.01$ , Fig. 5), illustrating that litter types that were strong CO<sub>2</sub> emitters were also strong CH<sub>4</sub> emitters. This correlation was also apparent in 135-d-old litter in the full sun treatment, but not in older litter or litter in the No UV/blue treatment (Appendix S1: Table S2). Emission of CO<sub>2</sub> at 70°C averaged  $\approx 50$  times higher than CH<sub>4</sub> in initial litter, as well as in most older litter (Appendix S1: Table S2). The only exception was in 135-d-old litter in the No UV/blue treatment, where the average ratio was

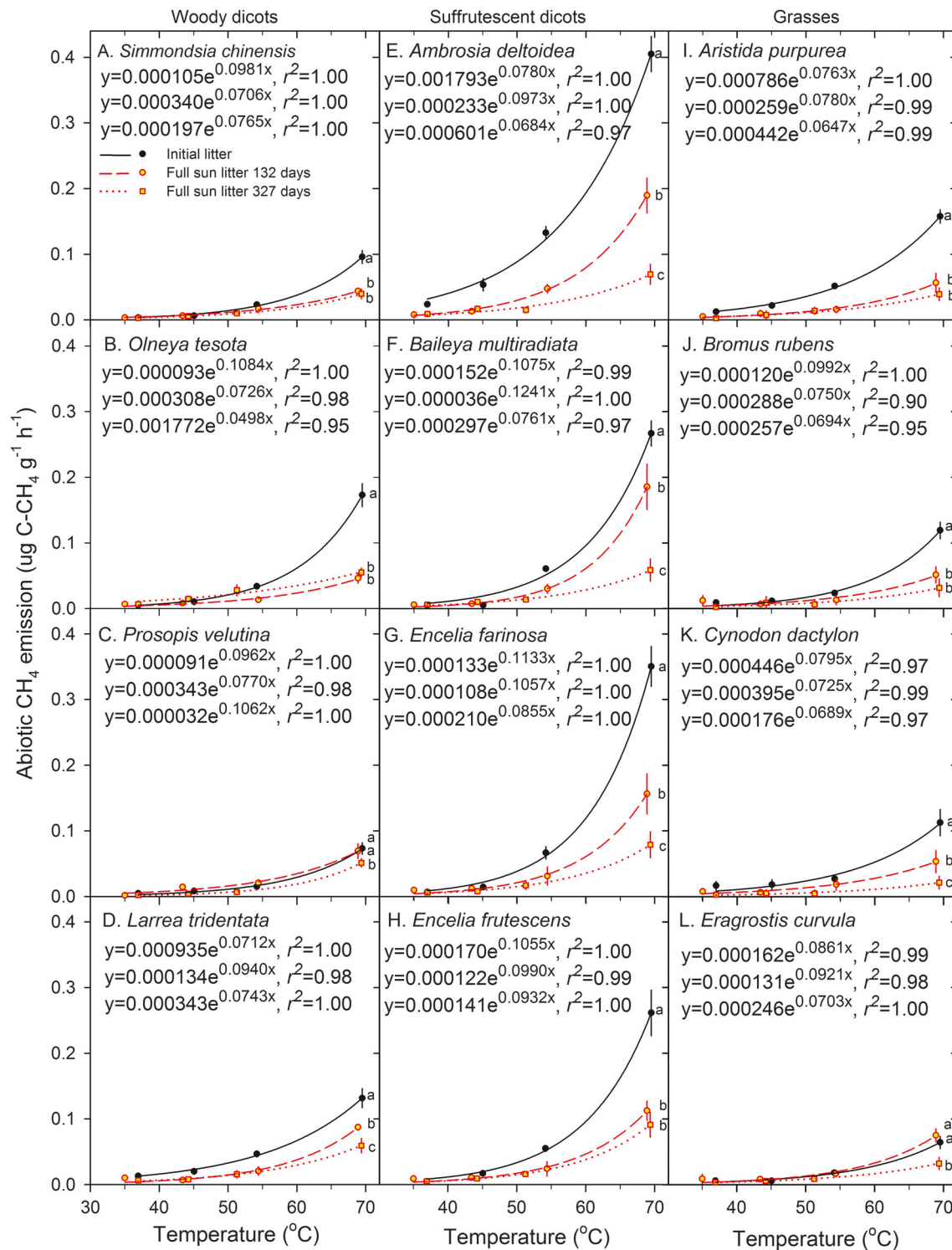


Fig. 4. Thermal response of abiotic  $\text{CH}_4$  emission from initial litter and litter in the full sun treatment after 135 and 327 d in the field. Values are mean  $\pm$  standard error ( $n=4$ ). Equations are fitted exponential functions. Different letters within a litter type denote significant differences in emission at  $70^{\circ}\text{C}$  ( $P \leq 0.05$ ).

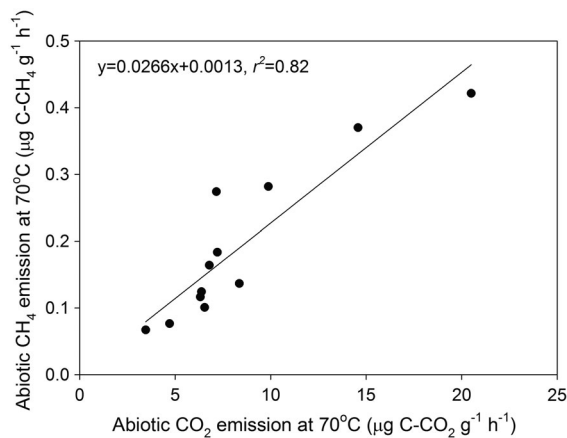


Fig. 5. Relationship between abiotic CO<sub>2</sub> and CH<sub>4</sub> emission of initial litter at 70°C. Values are means for each litter type ( $n = 4$ ). The linear regression was highly significant ( $P < 0.01$ ).

significantly higher (67.9) than other litter. Concerning growth-form effects, CO<sub>2</sub> and CH<sub>4</sub> emission (70°C) was greater from initial litter of suffrutescent dicots than grasses, while woody dicots were intermediate (Appendix S1: Fig. S4). The activation energy of thermal emission from initial litter averaged 102.5 kJ/mol (range: 74.8–120.9) for CO<sub>2</sub> and 84.2 kJ/mol (range: 53.0–118.0) for CH<sub>4</sub> (Appendix S1: Table S3).

#### What litter traits were correlated with emission?

Emission rates of both CO<sub>2</sub> and CH<sub>4</sub> at 70°C from initial litter were highly, positively correlated with concentrations of surface waxes ( $r^2 = 0.94$  and  $0.75$ , respectively), water-soluble fractions ( $r^2 = 0.52$  and  $0.76$ ), and DOC concentrations in these fractions ( $r^2 = 0.83$  and  $0.85$ ), when these traits were expressed on a litter surface-area basis (Table 1, Fig. 6). Emission rates of CH<sub>4</sub> were also positively correlated with ash ( $r^2 = 0.37$ , Table 1). Emission rates were also positively correlated with the same litter traits, when traits were expressed on a mass basis, with the exception of ash (Table 1). Because our aim was to assess the relevance of thermal emission to the total C loss of litter, we also examined correlations between initial emission and total C loss of litter (after 34 months); emission rates were not correlated with total C loss of litter ( $r^2 \leq 0.19$ ,  $P \geq 0.15$ ; Table 1), suggesting that thermal emission was not a dominant driver of litter C loss.

Table 1. Correlations between thermal emission rate of initial litter at 70°C and traits of initial litter, expressed on a 1-sided silhouette surface-area basis (upper values) and mass basis (lower).

Initial litter trait	Correlation with emission ( $r^2$ [P])	
	CO <sub>2</sub> emission	CH <sub>4</sub> emission
<b>Surface-area basis</b>		
Wax (mg/cm <sup>2</sup> )	+0.94 (<0.01)	+0.75 (<0.01)
Water solubles (mg/cm <sup>2</sup> )	+0.52 (<0.01)	+0.76 (<0.01)
Dissolved organic C (DOC) in solubles (mg/cm <sup>2</sup> )	+0.83 (<0.01)	+0.85 (<0.01)
Ash (mg/cm <sup>2</sup> )	+0.21 (0.14)	+0.37 (0.03)
C (mg/cm <sup>2</sup> )	+0.01 (0.82)	+0.00 (0.88)
N (mg/cm <sup>2</sup> )	+0.13 (0.26)	+0.10 (0.29)
Cellulose (mg/cm <sup>2</sup> )	−0.09 (0.32)	−0.06 (0.42)
Hemicellulose (mg/cm <sup>2</sup> )	−0.17 (0.19)	−0.17 (0.19)
Lignin (mg/cm <sup>2</sup> )	+0.00 (0.94)	+0.01 (0.84)
<b>Mass basis</b>		
Wax (%)	+0.89 (<0.01)	+0.62 (<0.01)
Water solubles (%)	+0.49 (<0.01)	+0.70 (<0.01)
DOC in solubles (%)	+0.77 (<0.01)	+0.72 (<0.01)
Ash (%)	+0.20 (0.13)	+0.48 (<0.01)
C (%)	−0.00 (0.92)	−0.15 (0.19)
N (%)	+0.04 (0.54)	−0.03 (0.62)
Cellulose (%)	−0.16 (0.20)	−0.14 (0.23)
Hemicellulose (%)	−0.22 (0.12)	−0.23 (0.11)
Lignin (%)	−0.00 (0.84)	−0.03 (0.57)
Specific leaf area (cm <sup>2</sup> /g)	−0.07 (0.40)	−0.09 (0.34)
Litter C loss in full sun (%)	+0.05 (0.48)	+0.12 (0.28)
Litter C loss in No UV/blue (%)	+0.13 (0.25)	+0.19 (0.15)

Notes: Values are coefficients of determination ( $r^2$ ) of linear regressions (and  $P$ -values in parentheses,  $n = 12$  litter types). Positive or negative correlations are denoted by + or − in front of  $r^2$ .

#### Emission from green leaves and compounds

To compare emission from dried green leaves, which was measured at 53°C, to emission from initial litter, we used the thermal emission equations for initial litter to estimate their emission at 53°C. Emission rates from initial leaf litter of *Prosopis velutina* and *Larrea tridentata* were significantly and substantially lower than from dried green leaves ( $P < 0.05$ , Appendix S1: Table S4). Specifically, emission rates of CO<sub>2</sub> and CH<sub>4</sub> from initial litter were only 9–44% (CO<sub>2</sub>) and 4–9% (CH<sub>4</sub>) of those from dried green leaves. Emission of CO<sub>2</sub> at 70°C from surface waxes and water-soluble compounds that we extracted from initial litter was greater than emission from pectins, cellulose, and xylan (Fig. 7A). The same was true for CH<sub>4</sub>, with the exception of water-soluble



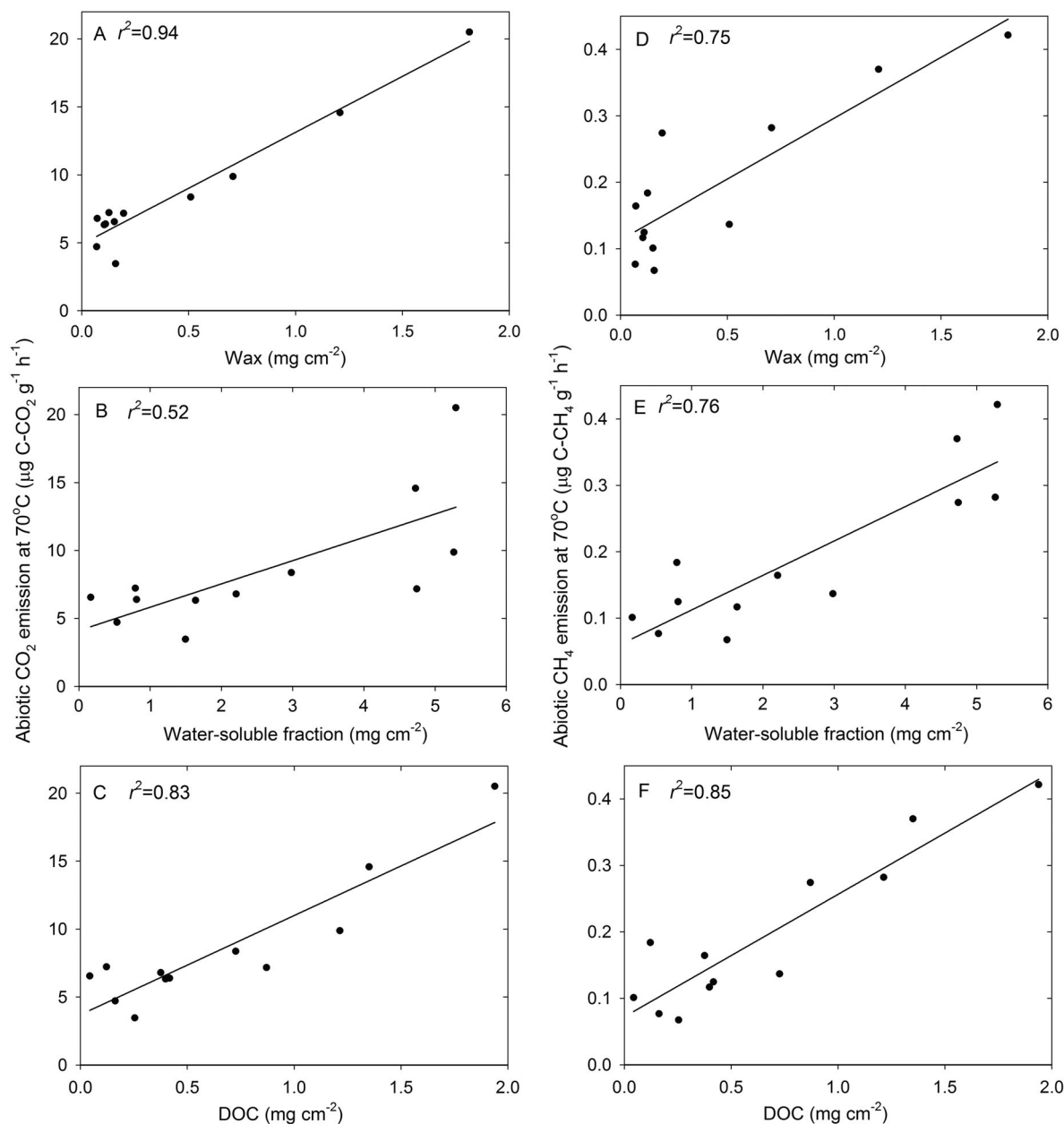


Fig. 6. Relationship between abiotic CO<sub>2</sub> (left) or CH<sub>4</sub> (right) emission of initial litter at 70°C and wax concentration (A or D), water-soluble fraction (B or E), and dissolved organic C concentration (C or F) of initial litter on a surface-area basis. Values are means of each litter type ( $n = 4$  for emission,  $n = 5$  for chemical traits), and lines are linear regressions; all correlations were highly significant ( $P < 0.01$ ).

compounds from *Baileya multiradiata*, whose emission was not greater than pectins (Fig. 7B). CO<sub>2</sub> and CH<sub>4</sub> emission from pectins was greater than emission from cellulose and xylan, which were both very low.

#### Litter temperatures in the field experiment

Over the entire field experiment, diel litter air temperature averaged 31.0°C and 30.0°C in the full sun and No UV/blue treatments, respectively, and diurnal temperatures averaged 39.8°C and

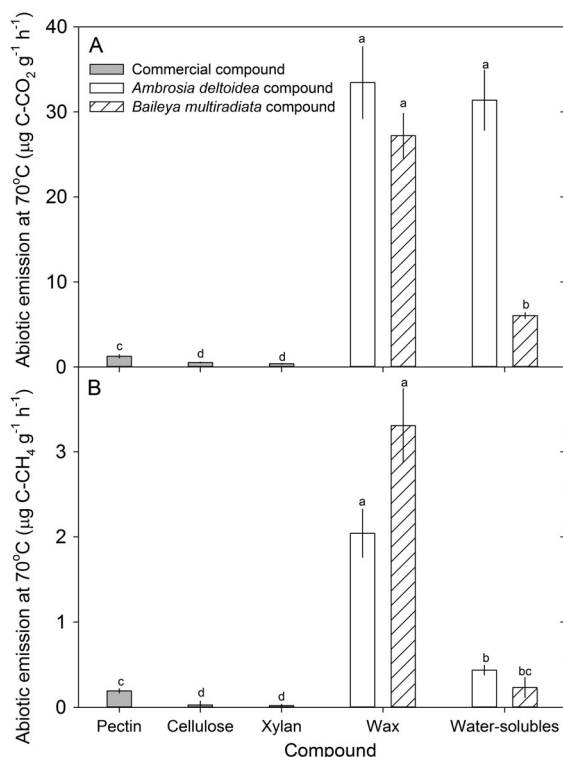


Fig. 7. Abiotic CO<sub>2</sub> (A) or CH<sub>4</sub> (B) emission rate at 70°C from commercial compounds (pectin, cellulose, and xylan, a form of hemicellulose), and waxes and water-soluble compounds extracted from initial litter of *Ambrosia deltoidea* and *Baileya multiradiata*. Values are mean  $\pm$  standard error ( $n = 4$ ). Bars with different letters within a panel are significantly different ( $P < 0.05$ ).

38.1°C in these treatments. Average monthly temperatures (diel) ranged from 11°C to 15°C in December and January, to 40–49°C in June through August (Fig. 8A, B). Litter temperatures occasionally exceeded 70°C in 15 of 34 months in the full sun treatment and 13 months in the No UV/blue treatment, and even exceeded 80°C in 5 months in the full sun treatment (Fig. 8A). Monthly mean temperature differences between the full sun and No UV/blue treatments were modest in the winter, with diel and diurnal differences usually <0.5°C and 1.5°C, respectively (Fig. 8C). In the summer, monthly mean temperature differences between treatments were much greater, particularly over diurnal periods when they averaged >2°C higher in the full sun in 11 of 34 months. In summary, temperatures were

consistently higher in the full sun than the No UV/blue treatment, and these differences were greatest during diurnal periods of warmer months.

#### Estimating thermal emission over the field experiment

Our first step in estimating thermal emission over the field experiment was to quantify the decline in emission with litter age (Fig. 2). We normalized the emission from different ages of each litter type, expressing them as a percentage of initial rates, and then modeled the average decline among all litter types with a 3-parameter exponential decay equation. These equations fit the average decline in emission with age well ( $r^2 = 1.00$ , Fig. 9). We also took into account that the decline in CO<sub>2</sub> emission with age was faster in litter in the full sun (Fig. 2A) by fitting separate decay equations to each radiation treatment (Fig. 9A). There was no difference in CH<sub>4</sub> emission decay between radiation treatments as litter aged (Fig. 2B), so we modeled this decay by pooling data from both treatments and assumed similar declines (Fig. 9B). Together with the equation for the thermal response of emission from initial litter of each type, this allowed us to use temperature to estimate emission rates from litter in each treatment as litter aged.

Emission from litter would also depend on the C content of litter, which declined through decay. We only measured C content of initial litter and litter at the 6th litter collection (634 d). We estimated the C content of litter over the entire field experiment by assuming that C loss paralleled organic dry-mass loss, which we measured at seven collections over the field experiment. This seems valid since litter C loss at 634 d was highly correlated with organic dry-mass loss at this time in both treatments ( $r^2 = 0.96$  and 0.90 for litter in full sun and No UV/blue treatments, respectively; Appendix S1: Fig. S5), and slopes and intercepts of these regressions were close to 1 and 0, respectively. To estimate the C content of each litter type on an hourly basis through the experiment, we assumed a linear decline in C content between each of the seven litter collections over the field experiment, which also seems valid, considering that linear decay models fit the dry-mass loss of all litter types well over the field experiment (Day et al. 2018). At each hour, we used litter

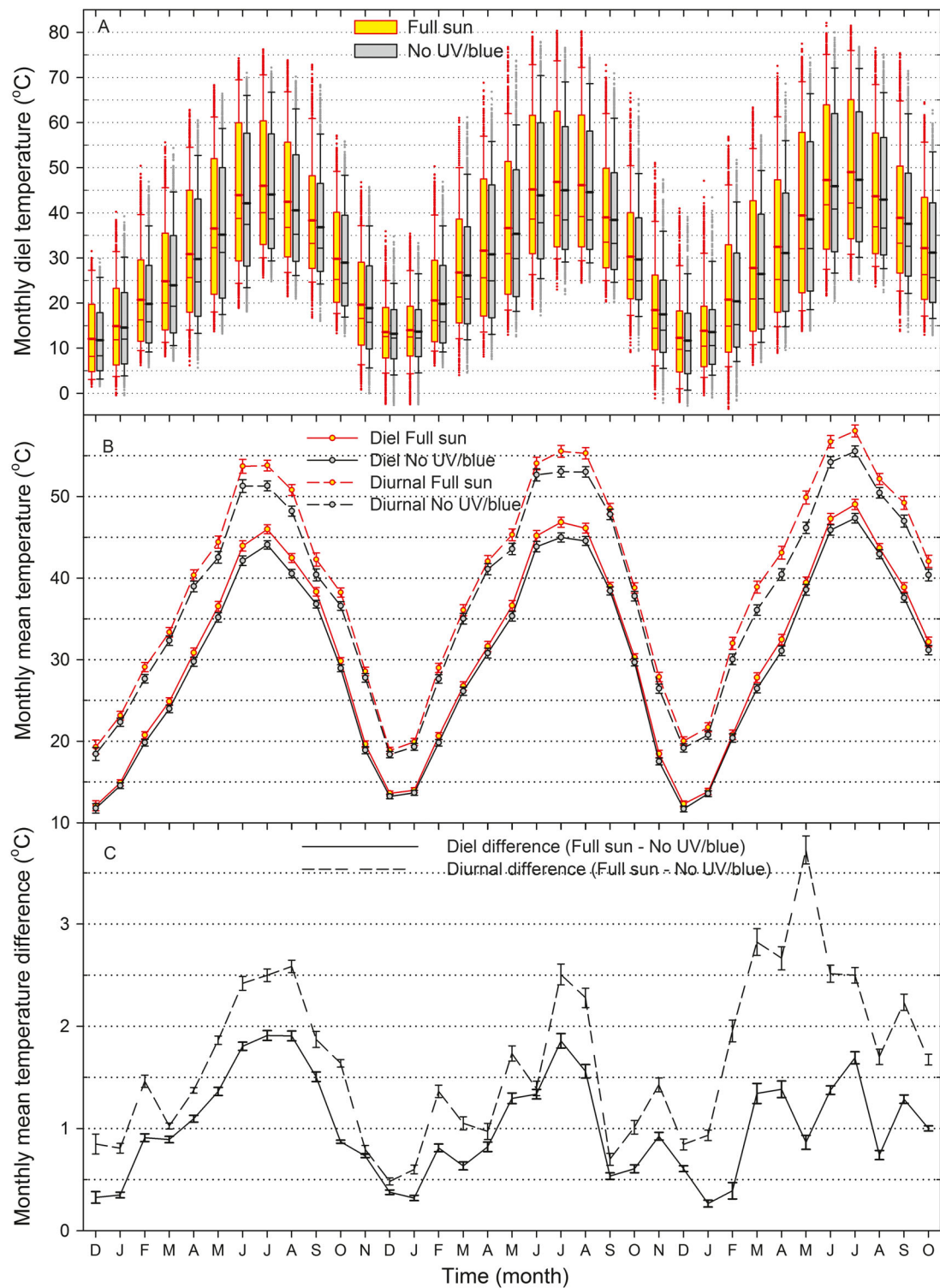


Fig. 8. (A) Diel litter temperatures, summarized as monthly box plots, from hourly measurements of litter in the full sun and No UV/blue treatments ( $n = 5$  sensors per treatment). The boundaries of each box are the 25th

(Fig. 8. *Continued*)

and 75th percentiles, and the thick and thin horizontal lines within each box are the mean and median, respectively. The error bars represent the 10th and 90th percentiles. Any hourly values above and below the latter error bars are shown as points. (B) Mean ( $\pm$ standard error [SE]) monthly diel and diurnal litter temperatures in the full sun and No UV/blue treatments. (C) Mean ( $\pm$ SE) monthly difference in diel and diurnal litter temperatures between the full sun and No UV/blue treatments.

temperature along with the thermal emission response and the C content of each litter type to estimate emission. Note that while we identified putative precursors to thermal emissions (i.e., surface waxes, water-soluble fractions, and DOC), we lack information on how these pools changed over decay and do not use this information in our emission estimates. Rather, declines in pools of these precursors would be an inherent part of the decline in emission that we measured and modeled as litter aged.

As expected, estimated monthly CO<sub>2</sub> emission in both treatments was greatest during warm months (Fig. 10). Emission was greater from litter in the full sun than the No UV/blue treatment during warmer months over the first year of the experiment, owing to higher litter temperatures. However, by the second year, CO<sub>2</sub> emission was lower from litter in the full sun and this pattern continued through the end of the experiment. Hence, the effect of the higher temperatures in full sun was overshadowed by the faster decline in CO<sub>2</sub> emission of this litter as it aged, along with the smaller pool of C remaining in this litter (i.e., litter in full sun decayed faster). On a cumulative basis, CO<sub>2</sub> emission from litter in the No UV/blue treatment exceeded that from litter in full sun by the second summer of the experiment in nearly all litter types, and this trend continued through the end of the experiment (Appendix S1: Fig. S6). Estimated monthly CH<sub>4</sub> emission was also highest during warm months over the experiment and greater from litter in the full sun than the No UV/blue treatment during warmer months over the first year (Fig. 11). Unlike CO<sub>2</sub>, CH<sub>4</sub> emission from litter in full sun remained greater over the second summer in most (10 of 12) litter types, which is not surprising considering that the decay in emission with litter age was similar in radiation treatments. By the third summer, CH<sub>4</sub> emission was slightly lower from litter in full sun in most (10 of 12) litter types, due to the smaller pool of C remaining in this litter. On a cumulative basis,

CH<sub>4</sub> emission from litter in full sun exceeded that from litter in the No UV/blue treatment throughout the experiment (Appendix S1: Fig. S7). In summary, higher temperatures in the full sun lead to higher emission rates of both CO<sub>2</sub> and CH<sub>4</sub> from this litter during the first summer of the experiment. However, total cumulative emission of CO<sub>2</sub> over the experiment was lower from litter in the full sun because emission rates and the C pool in this litter declined faster.

#### *Contribution of thermal emission to C loss*

The contribution of thermal emission of CO<sub>2</sub> and CH<sub>4</sub> to the total C lost from litter over the 34-month field experiment appeared very modest. Emission of CO<sub>2</sub> was responsible for an average loss of 0.8% of the original C in litter in the full sun and 1.0% in the No UV/blue treatment (Fig. 12A). Emission of CH<sub>4</sub> was responsible for an average loss of 0.03% of the original C in litter in both radiation treatments (Fig. 12B). The combined CO<sub>2</sub> and CH<sub>4</sub> emission was largely a function of CO<sub>2</sub> emission since this was much greater than CH<sub>4</sub>; combined emission of these gases was responsible for an average loss of 0.8% of the original C in litter in full sun and 1.0% of the original C in the No UV/blue treatment (Fig. 12C). Thermal emission losses were very modest relative to how much C was lost through all mechanisms: Litter in full sun lost on average 77.8% of its original C through all mechanisms, while litter in the No UV/blue treatment lost 60.8% of its original C (Fig. 12D). We estimate that thermal emission of these gases was responsible for an average of only 1.2 and 2.0% of the total C lost by litter in the full sun and No UV/blue treatments, respectively. In summary, thermal emission appeared to be a minor pathway of C loss over the experiment. Furthermore, total thermal emission losses were lower from litter in full sun, illustrating that this pathway could not be responsible for the greater C (or mass) loss observed in litter in the full sun treatment.



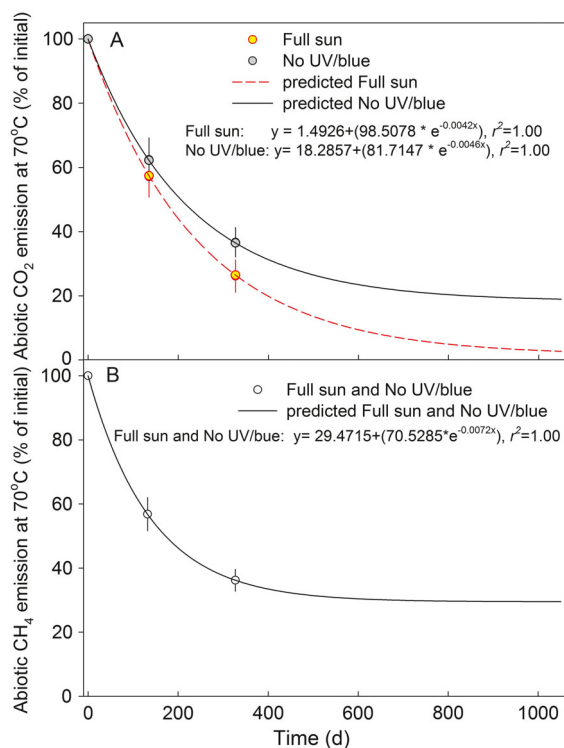


Fig. 9. Average change in CO<sub>2</sub> and CH<sub>4</sub> emission at 70°C of litter in full sun and No UV/blue treatments over time. CO<sub>2</sub> emission differed between full sun and No UV/blue treatments. Values through 327 d are means ( $n = 12$  litter types,  $\pm$  standard error). Lines are fitted exponential decay regressions. Values at the end of the experiment (1046 d) are predicted.

While thermal emission appeared to be a minor source of C loss over the entire field experiment, emission was greater from young litter, suggesting it might represent a more substantial pathway early in decay. Hence, we examined the contribution of thermal emission after 12 months in the field. The combined emission of CO<sub>2</sub> and CH<sub>4</sub> after 12 months was responsible for an average loss of 0.7% and 0.6% of the original C in litter in the full sun and No UV/blue treatments, respectively (Fig. 13A). These losses were modest compared to the total C lost (all mechanisms) after 12 months: Litter in the full sun lost 26.5% of its original C, while litter in the No UV/blue treatment lost 21.6% (Fig. 13B). From this, we estimate that thermal emission of these gases was responsible for an average of only 2.6% and 2.8% of the total C lost by litter after 12 months under the full

sun and No UV/blue treatments, respectively. Since we were ultimately interested in how thermal emission might confound our photodegradation assessment, we also expressed the difference in thermal emission C losses between the full sun and No UV/blue treatment as a percentage of the difference in total C losses (all mechanisms) between these treatments. Thermal emission accounted for an average of only 3% of the difference in total C lost by all mechanisms between the radiation treatments (Fig. 13C). Hence, photodegradation, rather than thermal emission, appeared to be the dominant mechanism responsible for the faster decay of litter in full sun over 12 months.

## DISCUSSION

The rates of thermal CO<sub>2</sub> and CH<sub>4</sub> emission we found and the exponential increase in these emissions with temperature are consistent with past reports on emission of these gases from plant material. Lee et al. (2012) found thermal emission rates at  $\approx 53^\circ\text{C}$  of CO<sub>2</sub> and CH<sub>4</sub> from dried green leaves of *Prosopis velutina* of  $\approx 25$  and  $0.2 \mu\text{mol C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , respectively. Expressing our rates from dried green leaves of this species in these units gives 12.7 and  $1.5 \mu\text{mol C}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , respectively. Keppler et al. (2006) found rates of  $0.4\text{--}5.3 \text{ ng CH}_4\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  from dried green leaves of several species at  $40^\circ\text{C}$ . Converting our rates to this temperature and units gives rates of  $1.0\text{--}32.1$  (average  $8.0$ )  $\text{ng CH}_4\cdot\text{g}^{-1}\cdot\text{h}^{-1}$  for initial litter. The exponential increase in emission of these gases we found is consistent with the findings of Lee et al. (2012) and Keppler et al. (2006) on dried green leaves of several species.

It seems unlikely that the source of the emissions we measured was microbial. At low temperature ( $22^\circ\text{C}$ ), which minimized thermal emission, we did not detect any CO<sub>2</sub> emission at the low relative humidity ( $\leq 20\%$ ) we used in our incubations. We did detect CO<sub>2</sub> emission in tests at  $22^\circ\text{C}$ , but only at high humidity ( $>70\%$ ), which we attribute to microbial respiration. This is consistent with the consensus that relative humidity above at least 60%, and 75% for most microbes, is required for sufficient moisture sorption and microbial activity (Nagy and Macauley 1982, de Goffau et al. 2009, Lebre et al. 2017). The exponential increases, and Arrhenius relationships, of

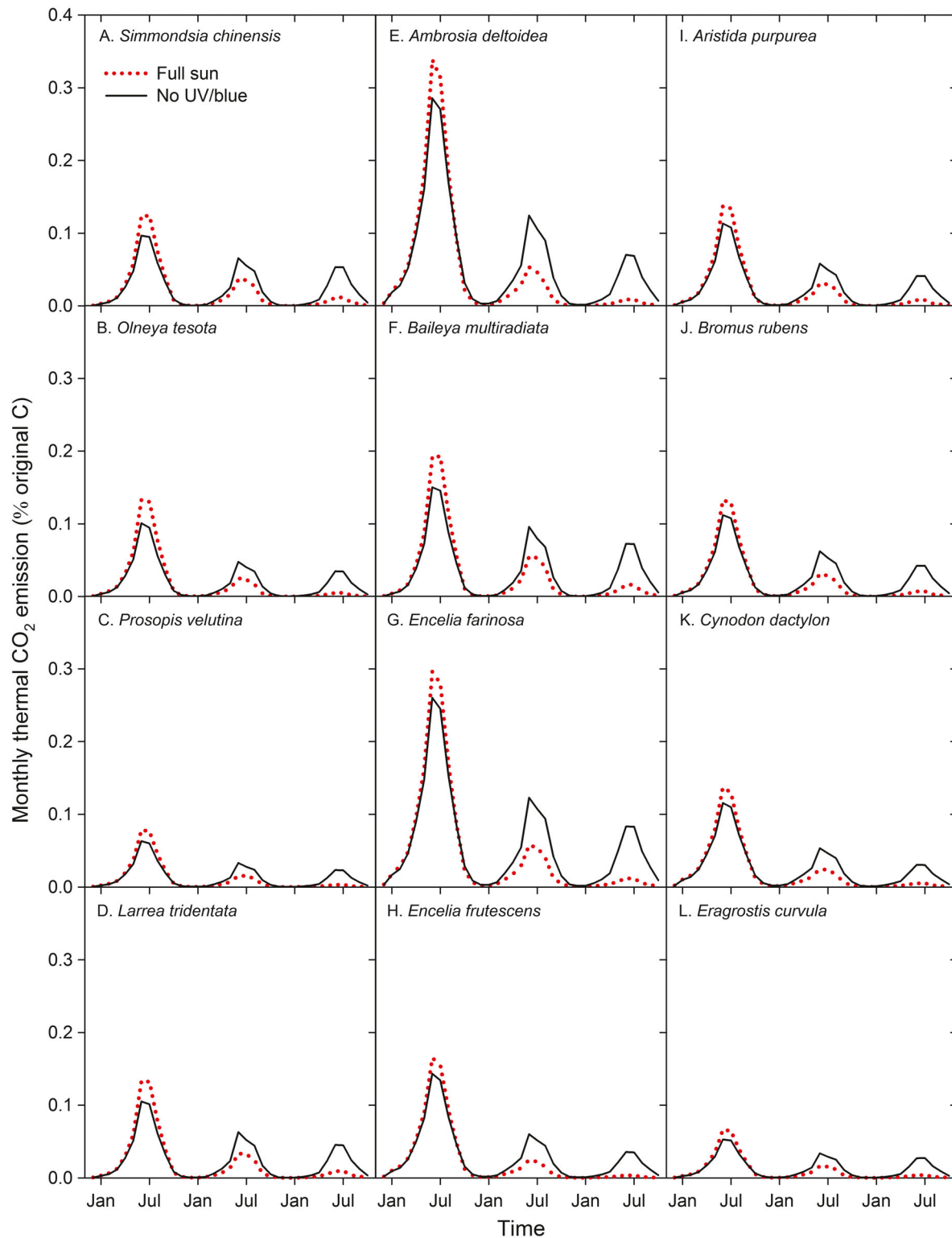


Fig. 10. Monthly thermal emission of CO<sub>2</sub> in full sun and No UV/blue treatments over the experiment, expressed as a percentage of the original C in initial litter.

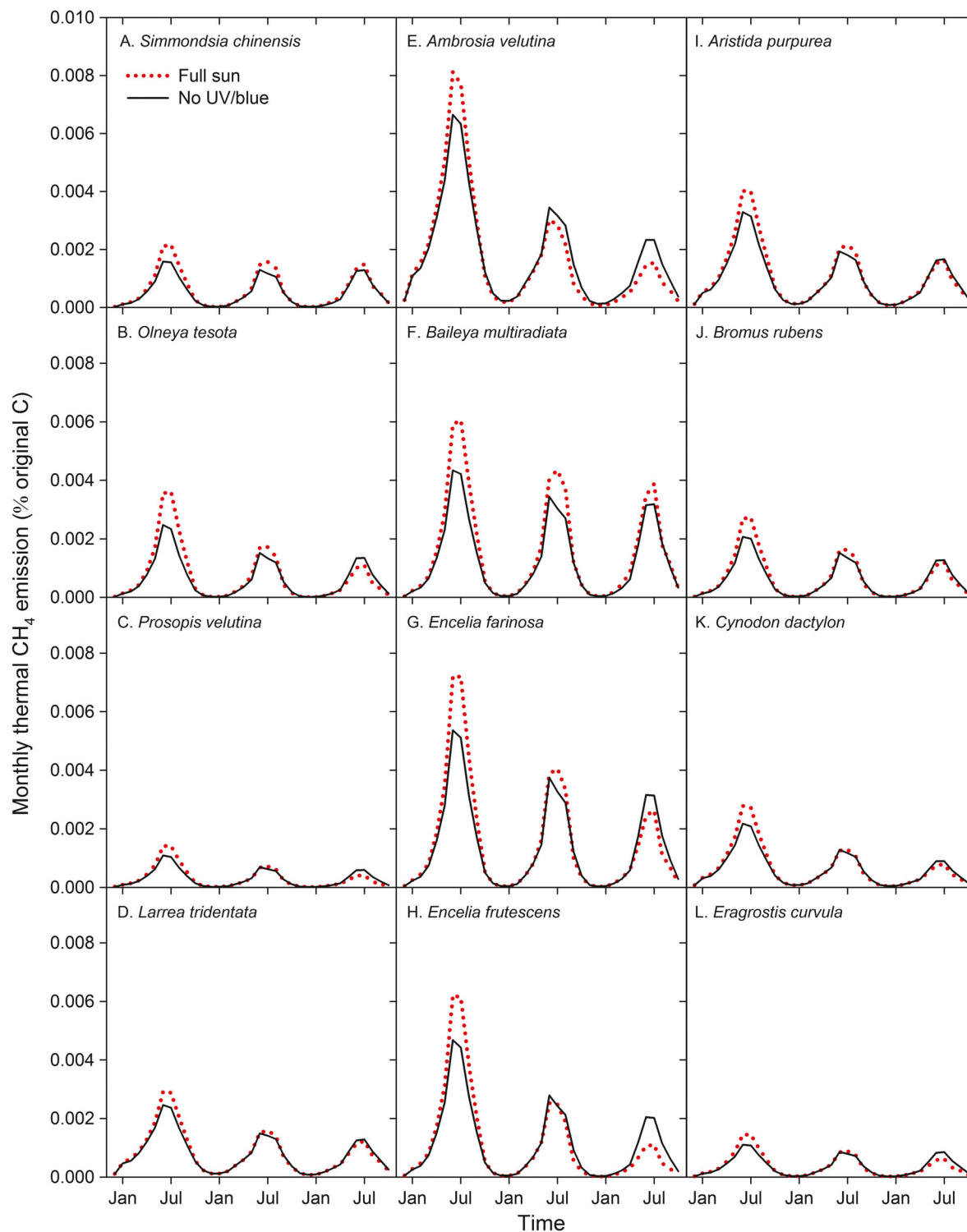


Fig. 11. Monthly thermal emission of  $\text{CH}_4$  in full sun and No UV/blue treatments over the experiment, expressed as a percentage of the original C in initial litter.

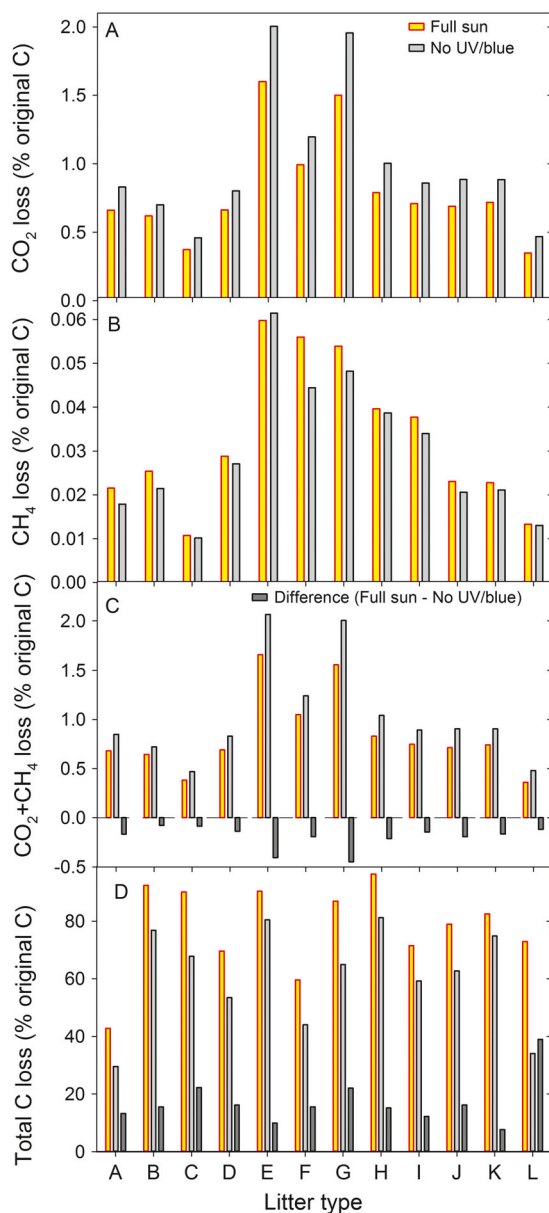


Fig. 12. Estimated C loss attributable to thermal CO<sub>2</sub> (A) and CH<sub>4</sub> (B) emission over the 34-month field experiment for litter in full sun and No UV/blue treatments, expressed as a percentage of original C in litter. The combined (sum) CO<sub>2</sub> and CH<sub>4</sub> emission, expressed as a percentage of the original C in litter in full sun and No UV/blue treatments, as well as the difference between these treatments (C). The observed total C loss (all mechanisms) of each litter type, expressed as a percentage of original C, over the field experiment in full sun and No UV/treatments, and the difference between these treatments (D). Refer to Fig. 1 for litter type codes.

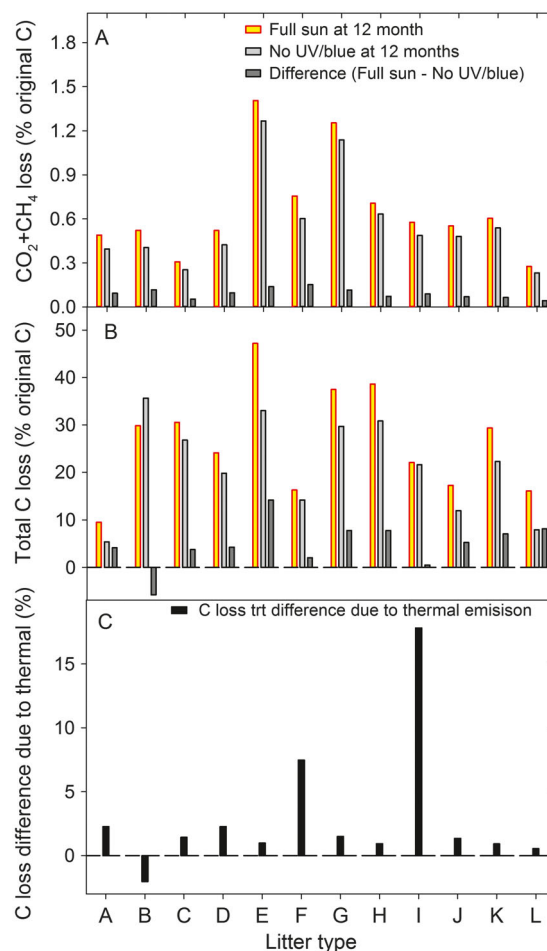


Fig. 13. Estimated C loss attributable to the combined abiotic thermal CO<sub>2</sub> and CH<sub>4</sub> emission after 12 months in the field experiment from litter in full sun and No UV/blue treatments, expressed as a percentage of original C mass of litter, along with the difference between treatments (A). The observed total C loss (all mechanisms) of each litter type, expressed as a percentage of original C mass, after 12 months in full sun and No UV/treatments, and the difference between treatments (B). The difference in C loss attributable to thermal abiotic emission between the full sun and No UV/blue treatments, expressed as a percentage of the difference in total C loss (all mechanisms) between these treatments, after 12 months (C). Refer to Fig. 1 for litter type codes.

thermal emission that we observed continued well above temperatures that most enzymes are thought to denature (45–50°C), also suggesting an abiotic source. Lastly, the high activation



energies ( $>50$  kJ/mol) we found are indicative of an abiotic, rather than biotic, process (Schönknecht et al. 2008). Hence, lack of litter moisture very likely prevented any microbial activity in our incubations. Outgassing of  $\text{CO}_2$  or  $\text{CH}_4$  from litter during our incubations also seems unlikely to be a dominant source of these gases. In preliminary tests, emission rates were similar regardless of whether we assessed this over incubations ranging from 4 to 24 h. Second, emission rates were strongly and positively correlated with surface wax concentrations; if outgassing were a major emission source, we would expect emission to be lower, not greater, from litter with greater wax concentrations, since waxes would impede the diffusion of gases from litter. Consistent with our contention, Kirschbaum and Walcroft (2008) and Vigano et al. (2008) concluded that outgassing was not a dominant source of  $\text{CH}_4$  emission.

Emission from initial litter was lower than from dried green leaves and declined exponentially as litter aged and decayed. This decline is consistent with a general decline in pools of precursors that would be expected through senescence and decay. Our findings illustrate that thermal emission rates of  $\text{CO}_2$  and  $\text{CH}_4$  from dried green leaves are unlikely to be a good proxy for emission from naturally senesced leaf litter (initial litter), and particularly from decaying litter, and would lead to substantial overestimates of litter emission. More work is needed to clarify how thermal, as well as photochemical, emission changes over leaf senesce and litter decay, and seems particularly warranted in the context of the ongoing debate as to whether aerobic  $\text{CH}_4$  emissions from leaves and litter represent a significant global flux (Keppler et al. 2006, Kirschbaum et al. 2006, Dueck and van der Werf 2008, Bloom et al. 2010, Carmichael et al. 2014, Fraser et al. 2015).

The strongest predictor of thermal emission from initial litter was surface wax concentration, which explained 94% and 75% of the variation among in  $\text{CO}_2$  and  $\text{CH}_4$  emission, respectively, among litter types. This relationship seemed very robust, as wax concentrations were also the strongest predictor of emission when traits were expressed on a mass basis. Consistent with this, emission from waxes we extracted from litter was higher than from other putative precursors such as pectin, cellulose, and xylan. Consistent with

our findings, Bruhn et al. (2014) found that surface waxes are a source of UV photochemical emission of  $\text{CH}_4$  from live leaves. Our results strongly suggest that surface waxes are also precursors of thermal emission of  $\text{CH}_4$ , as well as  $\text{CO}_2$ . This seems consistent with the decline in emission rates we observed over leaf senescence and litter decay. Surface waxes would likely be among the compounds lost earliest in decay, as they would be prone to abrasion, leaching, photochemical emission, and microbial degradation. Along with waxes, water-soluble fractions and the DOC concentration in these fractions were also strongly correlated with emissions. These fractions contain a diverse group of compounds making the identity of precursors unclear. While pectins have received considerable attention as a precursor of  $\text{CH}_4$  emission from leaves (Keppler et al. 2006, 2008, McLeod et al. 2008, Vigano et al. 2008, Bruhn et al. 2009, Messenger et al. 2009, Hurkuck et al. 2012), an examination of the stable isotope signatures of  $\text{CH}_4$  emitted from plant material and compounds suggested that there are likely multiple sources for photochemical emission of  $\text{CH}_4$  (Vigano et al. 2009). Lignin is another precursor of thermal emission of  $\text{CO}_2$  and  $\text{CH}_4$ , and Hurkuck et al. (2012) found much higher emission from lignin than pectin. We did not assess emission from purified lignin; we chose not to because of uncertainties regarding potential structural changes, as well as impurities, which could occur during the extraction/purification process. The same caveat would also pertain to all the compounds that we did assess, although lignin may represent a worse case because of the relatively extreme chemical conditions used to extract it (Hatfield and Fukushima 2005, Sluiter et al. 2010, Preston and Trofymow 2015). In any case, this caveat complicates the comparison of emission rates from the different compounds that we assessed.

Thermal emission of  $\text{CO}_2$  and  $\text{CH}_4$  appeared strongly coupled, particularly in initial litter. Lee et al. (2012) found a similar correlation and suggested that some of the  $\text{CH}_4$  may quickly oxidize to  $\text{CO}_2$ . However, another possibility is simply that these gases share some of the same precursors, which seems likely based on the strong correlations we found between emissions of both gases and the same litter compounds. This latter possibility is also consistent with the recent findings of Althoff et al. (2014) and Benzing et al.

(2017) on the chemistry of methane formation under aerobic conditions.

Thermal emission appeared to represent a very minor pathway of C loss from litter. For example, thermal emission accounted for only 1.2% and 2.0% of all C lost from litter in the full sun and No UV/blue treatments, respectively, over the field experiment. Even over the first year of the experiment, when emission was greatest, it accounted for only 2.6% and 2.8% of the all C lost in these treatments. This contention that thermal emission was a minor loss pathway is corroborated by the lack of correlation between thermal emission rates and total C loss from litter. We only assessed CO<sub>2</sub> and CH<sub>4</sub>, and thermal emission of other C-based trace gases (e.g., CO, C<sub>2</sub>H<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub>), as well as N-based trace gases (McCalley and Sparks 2009), from litter is likely. However, Lee et al. (2012) and King et al. (2012) concluded that CO<sub>2</sub> is the primary C-based trace gas produced by litter during thermal degradation, and it seems unlikely that the inclusion of these other trace gases would increase the relative contribution of thermal emission to the extent that it would be a substantial pathway of C or mass loss from litter. We measured thermal emission under low relative humidity to ensure that microbial sources were negligible. Hurkuck et al. (2012) found that adding water to lignin, pectin, or soils increased thermal CH<sub>4</sub> emission rates. Hence, it is conceivable that thermal emission from litter could be greater under higher humidity or wet field conditions, such that we have underestimated the role of abiotic thermal emission in litter C loss. However, microbial emission could very well be appreciable under these conditions, and distinguishing abiotic from microbial sources could prove challenging.

Our findings strongly suggest that thermal emission did not confound our field photodegradation assessment or prior conclusion that photodegradation was a significant driver of litter mass or C loss (Day et al. 2018). Not only did thermal emission represent a very modest pathway for C loss from litter, but cumulative emission was actually greater from litter in the No UV/blue than the full sun treatment over the experiment. Hence, the influence of higher litter temperatures in the full sun treatment was overshadowed by the faster decline in CO<sub>2</sub> emission of this litter, along with faster decline in the C pool available for emission

in full sun. Indirect evidence corroborating our idea that thermal emission did not contribute to the greater C loss of litter in full sun comes from the contrasting temporal patterns of thermal emission vs. photodegradation: The contribution of thermal emission declined appreciably as litter aged, whereas the magnitude of photodegradation increased over this field experiment (Day et al. 2018), as well as a past experiment at the same site (Day et al. 2015).

In field filter experiments assessing photodegradation, the greater solar irradiance received by litter and the surrounding soil/vegetation surface under transparent filters would likely lead to higher litter temperatures than those under filters absorbing solar radiation. Some studies have documented elevated temperatures under transparent filters, particularly during summer periods (Austin and Vivanco 2006, Day et al. 2015, 2018), although many have reported no significant temperature differences, which we suspect stems in some cases from small replication size. In any case, the magnitude of these elevated temperatures would depend on the specific filters used (e.g., which wavebands and how much solar radiation was filtered) and their design (e.g., height and shape of filters and their influence on air mixing). These factors vary substantially among past photodegradation assessments, making generalizations about temperature differences difficult. Our system represents a high thermal emission environment for surface litter because of high ambient air temperatures and solar irradiance, which promotes surface heating. Not surprisingly, litter temperatures under our transparent filters averaged 39.8°C over our field experiment, generally consistent with findings from other Sonoran Desert sites (Predick et al. 2018), and temperatures occasionally exceeded 75°C in several months in both radiation treatments. Our system probably also represents a worst-case scenario in terms of the confounding effects of temperature and thermal emission in photodegradation assessments, because high solar irradiance would promote elevated temperatures under transparent filters. Indeed, diurnal litter temperatures averaged 1.7°C higher under transparent filters over the experiment. Nevertheless, our analysis strongly suggests that thermal emission did not confound our conclusion that photodegradation was a

substantial driver of litter mass and C loss, and suggests that the same would be true for field assessments in most other systems.

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