



Differential effects of redox conditions on the decomposition of litter and soil organic matter

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Abstract Soil redox conditions exert substantial influence on biogeochemical processes in terrestrial ecosystems. Humid tropical forest soils are often characterized by fluctuating redox, yet how these dynamics affect patterns of organic matter decomposition and associated CO₂ fluxes remains poorly understood. We used a ¹³C-label incubation experiment in a humid tropical forest soil to follow the decomposition of plant litter and soil organic matter (SOM) in response to four redox regimes—static oxic

or anoxic, and two oscillating treatments. We used high-resolution mass spectrometry to characterize the relative composition of organic compound classes in the water extractable OM. CO₂ production from litter and SOM showed different responses to redox treatments. While cumulative production of SOM-derived CO₂ was positively correlated with the length of oxic exposure ($r = 0.89$, $n = 20$), cumulative ¹³C-litter-derived CO₂ production was not linked to oxygen availability. Litter-derived CO₂ production was highest under static anoxic conditions in the first half of the experiment, and later dropped to the lowest rate amongst the treatments. In anoxic soils, we observed depletion of more oxidized water-extractable OM (especially amino sugar-, carbohydrate-, and protein-

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like compounds) over the second half of the experiment, which likely served as substrates for anaerobic CO₂ production. Results from two-pool kinetic modeling showed that more frequent anoxic exposure limited decomposition of a slow-cycling C pool, but not a fast-cycling pool. These results suggest that aerobic and anaerobic heterotrophs were equally effective at degrading labile substrates released from fresh plant litter in this humid tropical forest soil, while aerobic decomposers were more effective in breaking down the potentially refractory compounds found in SOM.

Keywords Luquillo Experimental Forest · Puerto Rico · Redox oscillation · Soil respiration · Soil organic matter · ¹³C isotope tracing · Decomposition · FTICR-MS

Introduction

Tropical forests have some of the highest litter decomposition rates among terrestrial biomes (Parton et al. 2007) and are important sources of greenhouse gases, including carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) (Kirschke et al. 2013; Hashimoto et al. 2015). Ongoing changes in climate have already affected the carbon (C) balance of tropical forests by altering their temperature and rainfall regimes and thus soil moisture, microbial community and redox patterns (O’Connell et al. 2018). However, the effects of these changes on ecosystem biogeochemistry are not well understood and poorly represented in ecosystem models.

Reduction–oxidation (redox) reactions are important drivers of decomposition and greenhouse gas emissions, particularly in warm, wet, fine-textured tropical soils. Oxygen (O₂) is a preferred terminal electron acceptor, and critical for the deconstruction of macromolecular organic compounds, since the most powerful enzymes—oxidases and peroxidases—can only be used if O₂ is available (Sinsabaugh 2010). Thermodynamic considerations predict that decreased O₂ availability should limit a soil’s CO₂ production rate (Greenwood 1961) and many modern biogeochemical models include a dimensionless scaling factor (r_{oxygen}) to account for decreased decomposition rates under anoxic conditions (Koven et al. 2013;

Riley et al. 2014). Although upland soils are often presumed to be well-aerated, many studies illustrate the prevalence of temporary hypoxic and anoxic conditions in upland soils, at spatial scales ranging from aggregates to the entire soil profile (Silver et al. 1999; Schuur et al. 2001; Fimmen et al. 2008; Hall et al. 2016a; Keiluweit et al. 2018), with impacts on multiple biogeochemical processes (Pett-Ridge and Firestone 2005; Pett-Ridge et al. 2006; Keiluweit et al. 2017; Chen et al. 2018). Intriguingly, some lab and field studies of tropical soils report similar CO₂ emission rates during both oxic and anoxic periods (Teh et al. 2005; DeAngelis et al. 2010; Liptzin et al. 2011; Bhattacharyya et al. 2018), highlighting the need to better understand the parameters that regulate redox sensitivity of SOM decomposition.

When O₂ is limiting, soil microorganisms must use alternative terminal electron acceptors to oxidize SOM. Iron (Fe) reduction is a particularly important anaerobic respiration pathway in tropical soils, given the abundance of Fe minerals and Fe reducers in these environments (Dubinsky et al. 2010; Ginn et al. 2017). The activity of Fe reducers and most anaerobes is strongly influenced by the chemical composition of their organic substrates, since the biogenic yield from oxidation of a given organic compound can be linked to its nominal oxidation state of C (NOSC) (Jin and Bethke 2003; Masiello et al. 2008). For example, reduced substrates such as alkenes and lipids (low NOSC values) should not provide enough bioenergetic yield to be coupled with Fe reduction, whereas more highly oxidized substrates such as simple organic acids (high NOSC values) can be readily oxidized by both Fe reducers and aerobic microorganisms (Keiluweit et al. 2016). Therefore, substrate molecular composition likely regulates how the decomposition of SOM responds to dynamic redox conditions. As oxygen-rich compounds are more enriched in fresh litter and root exudates than in mineral soil (Masiello et al. 2008), anaerobes may preferentially use plant-derived C during early stages of decomposition. However, little is known about the redox sensitivity of litter versus SOM decomposition in upland environments.

We used a laboratory incubation experiment to explore the effects of static and dynamic redox regimes on plant litter versus SOM decomposition and CO₂ production using a tropical forest soil. Two fluctuating redox regimes (high vs low frequency)

were imposed in soil microcosms, in addition to static oxic and anoxic regimes. ^{13}C -enriched leaf litter added to the soil incubations allowed us to partition CO_2 fluxes into two sources, litter and SOM. Gas fluxes were assimilated into a two-pool decomposition model, where we compared redox effects on decomposition of a fast-cycling versus a slow-cycling C pool. We also characterized the chemical composition of water-extractable OM using high-resolution mass spectrometry over the course of the experiment. We hypothesized that O_2 availability would regulate the decomposition of both litter and SOM and predicted that CO_2 production from both sources would positively correlate with the length of oxic headspace exposure.

Materials and methods

Experimental design

Surface soils (0–10 cm) (Humic Haploperox, Soil Survey Staff 1995) were collected from near the El Verde field station in the Luquillo Experimental Forest (LEF), Puerto Rico, a NSF Long-Term Ecological Research site and Critical Zone Observatory. The location is on a 15% slope where soil O_2 fluctuations are common (Bhattacharyya et al. 2018; O'Connell et al. 2018); prior work in this forest suggests that microbial communities are adapted to redox oscillations that occur approximately every 4–6 days (Pett-Ridge and Firestone 2005; Pett-Ridge et al. 2006, 2013; DeAngelis et al. 2010). The study site is described locally as a Tabonuco (*Dacryodes excels* Vahl) forest, in the subtropical wet forest life zone (Ewel and Whitmore 1973). Mean annual temperature was 23 °C, and mean annual precipitation was 3.5 m that was relatively evenly distributed throughout the year (Scatena 1989). The average soil pH, clay content, C concentration, and oxalate-extractable Fe concentration were 5.6, 20%, 6.1%, and 5.9 mg g⁻¹ soil, respectively (Bhattacharyya et al. 2018; O'Connell et al. 2018).

Soils were shipped overnight, gently homogenized, and divided for incubation as described in Bhattacharyya et al. (2018). Approximately 20 g (oven dry weight equivalent, ODE) of soil was weighed into each of 44 glass microcosms (487 ml). Twenty 'trace gas' microcosms (5 per treatment) were repeatedly

monitored for CO_2 production and destructively harvested at the end of the experiment; additional replicate microcosms were harvested during the experiment. For the initial 16 days, all microcosms were exposed to a 4-day oxic (flushing with medical grade air)/4-day anoxic (flushing with N_2) pre-incubation period to allow soil respiration to stabilize.

After the pre-incubation period, all microcosms were amended with 180 mg ^{13}C -labeled ground ryegrass litter (97 atom%, Isolife, Wageningen, Netherlands; ~ 6% of the soil's native C content) and incubated for 44 days. Microcosms were split into four redox treatments, managed via headspace manipulation: (1) static anoxic (N_2 gas), (2) static oxic (medical air), (3) 4 days oxic/4 days anoxic (high frequency), (4) 8 days oxic/4 days anoxic (low frequency) (Fig. S1). Both high and low frequency treatments started and ended with oxic phases. In a companion study, we used unlabeled litter with the same experimental design to explore coupled cycling of Fe and C geochemistry (Bhattacharyya et al. 2018), and soil P dynamics (Lin et al. 2018).

Trace gas sampling and measurement

Headspace samples were collected approximately every 4 days from the 20 trace gas microcosms (4 redox regimes \times 5 replicates) to assess fluxes of CO_2 and ^{13}C - CO_2 concentrations. For fluctuating treatments, microcosms were sampled immediately before the redox conditions were altered. To measure CO_2 fluxes, microcosms were temporarily sealed for 2 h, and gas samples were collected at the beginning and end of the sealed period by removing 30 ml of the headspace via septa into pre-evacuated 20 ml glass vials. Microcosms were sealed for 3 h when CO_2 production rates decreased towards the end of the experiment. CO_2 concentrations were measured on a gas chromatograph (GC-14A, Shimadzu, Columbia, MD), equipped with a thermal conductivity detector. CO_2 fluxes were determined by calculating the concentration difference during the sealed period, assuming a linear flux rate. An extra set of gas samples collected from each microcosm after the sealed period was analyzed for the $^{13}\text{C}/^{12}\text{C}$ CO_2 isotope ratio with an isotope ratio mass spectrometer (IRMS; IsoPrime 100, Elementar, Hanau, Germany). We also monitored CH_4 production during the experiment and found that cumulative CH_4 production was trivial compared to

CO₂, with no apparent redox treatment effect (Fig. S2).

Microcosm harvests and chemical analysis

Soil microcosms were destructively harvested at three timepoints during the experiment, on days 20 and 36 ($n = 3$ per treatment each day) and day 44 ($n = 5$ per treatment, the trace gas microcosms). For the middle timepoint, samples from the low-frequency treatment were harvested on day 33 instead of day 36. This ensured that samples from both fluctuating treatments were all collected under an oxic headspace throughout the experiment (Fig. S1). For the ease of comparison, we analyzed the chemical data of the low-frequency treatment collected on day 33 along with data of other treatments collected on day 36. Samples exposed to an oxic headspace preceding the harvest were processed on the benchtop; those finishing an anoxic period were processed in an anoxic glove box (Coy Laboratory Products, Grass Lake, MI). Dissolved organic C (DOC) was extracted by shaking 2 g of soil (ODE) in 200 ml of Milli-Q water for 1 h and then passing through a 0.45 μm filter. DOC concentrations were measured with a Total Organic Carbon Analyzer (TOC-VCSH, Shimadzu). Background soil and litter ¹³C/¹²C isotope ratios were measured with a Vario Micro elemental analyzer (Elementar, Hanau, Germany) in-line with the IRMS (Table S1).

From each harvested microcosm, a soil subsample was frozen and sent to the Environmental Molecular Sciences Laboratory (Richland, WA) for Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS) analysis of OM composition, following the approach of Tfaily et al. (2017). Briefly, 100 mg of soil (ODE) was sequentially extracted with water, methanol, and chloroform to extract polar and nonpolar extractable OM. Soil was shaken with each solvent (2 ml) for 2 h on an Eppendorf Thermomixer and centrifuged before collecting the supernatant. Water extracts were then desalted by solid phase extraction using Varian PPL cartridges according to Dittmar et al. (2008). Our analyses showed that redox treatment did not significantly affect the composition of methanol- or chloroform-extractable OM, thus, we focused on the results of water-extractable OM, which we expect is more relevant to the processes naturally occurring in wet tropical forest soils.

A 12 T Bruker Solarix FTICR mass spectrometer was used to collect high resolution mass spectra of the organic compounds in the extracts. Electrospray needle voltage and Q1 were set to + 4.4 kV and m/z 50, respectively, with 144 scans averaged per sample. Ion accumulation time was optimized for all samples to account for differences in DOC concentration (Boye et al. 2017). Mass spectral peaks were internally calibrated using a commonly identified OM homologous series where each member differs from the next/previous by one $-\text{CH}_2$ group or 14 mass units (Da). The mass measurement accuracy was within 1 ppm for singly charged ions across the range 200–800 m/z . Peaks were extracted with DataAnalysis software (Bruker, Billerica, MA) using the following: signal to noise threshold ≥ 7 , relative threshold base peak = 0.01, absolute intensity threshold = 100, and m/z range of 200–750. Means and standard errors for the numbers of water-extractable molecular formulae are presented in Table S2 per sampling day and treatment. Samples with low peak yield (< 200 peaks; $n = 4$), likely due to high Fe levels that distorted ionization, were excluded from further analysis. The high frequency treatment on day 20 was excluded from our analysis as two of three samples returned low numbers of peaks. Molecular formulae were assigned with EMSL's in-house software, Formularity, based on the Compound Identification Algorithm (CIA) (Kujawinski and Behn 2006; Tolić et al. 2017). Spectral data were processed with the R package 'ftmsRanalysis' ($n = 38$) (Bramer et al. 2020). Our analysis did not focus on ¹³C-labeled compounds as many litter-derived by-products are expected to be low-molecular-weight compounds (e.g., acetate, glucose, and amino acids) that are not normally detected with electrospray ionization FTICR-MS.

Modeling total CO₂ fluxes

To evaluate the effects of redox pattern on decomposition rates, we fitted total CO₂ fluxes (without isotopic partitioning) from each treatment and time point to a two-pool model with three coefficients (Sierra and Markus 2015). This model assumes that soil organic C is comprised of two distinct pools with different decomposition rates following first-order kinetics:

$$\frac{dC}{dt} = -k_1 * C_1 - k_2 * C_2$$

$$C_1 = \gamma * C_0$$

where the total C in the microcosm was made of “fast-cycling” and “slow-cycling” pools (C_1 and C_2 , respectively), with corresponding decomposition constants k_1 and k_2 ($k_1 > k_2$), expressed as day^{-1} . We used the ‘fast-cycling’ and ‘slow-cycling’ convention, while acknowledging that organic matter is more realistically represented by a continuum of material with different cycling rates (Waring et al. 2020). The initial C content (C_0) was partitioned into C_1 and C_2 using the coefficient γ . We did not use isotopic data in this part of the analysis, and model-derived partitioning between fast-cycling and slow-cycling pools is independent of that between litter- and SOM-derived organic matter. The fast-cycling pool primarily contributes to the initial CO_2 flux peak, while the slow-cycling pool accounts for the CO_2 flux after it stabilizes later in the incubation. Because the values of all three model coefficients varied amongst redox treatments, we independently compared redox effects on the size of fast-cycling and slow-cycling pools and their degradability. Model coefficients were estimated using a two-step procedure described in Soetaert and Petzoldt (2010). First, an initial approximation to the coefficients values was estimated by optimizing a cost function based on the sum of squared residuals of coefficients weighed by the number of observations. Functions ‘modCost’ and ‘modFit’ from the R package ‘FME’ were used to construct the cost function and derive coefficients estimates. Second, the estimated coefficients and covariance matrix were used as priors for a Bayesian optimization procedure using Markov chain Monte Carlo with the function ‘modMCMC’. A total of 20,000 iterations were run with a burn-in of 1000 iterations. We report mean estimates and standard deviations of each coefficient obtained from the Bayesian procedure (Sierra et al. 2017).

Data analysis

The percent contribution of ^{13}C litter (P_{litter}) to the total CO_2 flux was calculated using a linear mixing model:

$$P_{\text{litter}} = 100 * \frac{\chi(^{13}\text{C})_{\text{flux}} - \chi(^{13}\text{C})_{\text{SOM}}}{\chi(^{13}\text{C})_{\text{litter}} - \chi(^{13}\text{C})_{\text{SOM}}}$$

Here, $\chi(^{13}\text{C})_{\text{flux}}$ represents the measured ^{13}C atom% of the CO_2 flux. Variables $\chi(^{13}\text{C})_{\text{litter}}$ and $\chi(^{13}\text{C})_{\text{SOM}}$ refer to labeled litter and SOM measured atom% (97.0 and 1.08 atom%, respectively; Table S1). Calculations were conducted per microcosm, allowing us to estimate the errors of P_{litter} . Flux rates were assumed to change linearly between two sampling days, and cumulative gas fluxes were calculated by integrating over the 44-day period (area under the curve). Treatment effects on cumulative gas fluxes were examined with analysis of variance (ANOVA) followed by Tukey’s tests using R package ‘emmeans’ (Lenth 2019). Treatment effects on CO_2 fluxes were also assessed with this approach on each sampling day.

We used regression models to evaluate headspace condition (oxic vs. anoxic) effects on CO_2 fluxes in the two fluctuating redox treatments. Since litter-derived CO_2 production had a strong decreasing trend, its regression model included three terms: the decreasing trend [modeled with a quadratic polynomial function of time (Diggle et al. 2002)], the effects of headspace redox conditions, and an error term. Preliminary analysis suggested the decreasing trend alone explained of 66% and 73% of variability in the high-frequency and low-frequency treatment, respectively. We assessed autocorrelation between measurements made from the same microcosm by designating its effect as a random intercept term; however, this did not improve model fit. Therefore, microcosm was not included in the regression model. Because SOM-derived CO_2 production did not show a clear temporal trend, we treated time as a random intercept in the model along with the effects of redox and error. We did not include microcosm effects because model fit was not improved.

We used Nonmetric Multidimensional Scaling (NMDS) to visualize redox treatment effects on OM composition, using FTICR-MS peak heights converted to presence/absence data. NMDS was conducted with the R ‘vegan’ package based on Jaccard distance (Oksanen et al. 2019) and assessed with a permutational multivariate ANOVA (PERMANOVA) using the ‘adonis’ function.

Using the stoichiometry of assigned formulae, the NOSC value was calculated for each FTICR-based

mass peak following the equation (Masiello et al. 2008; LaRowe and Van Cappellen 2011):

$$NOSC = 4 - \frac{-Z + 4C + H - 3N - 2O + 5P - 2S}{C}$$

where Z corresponds to the compound's net charge (assumed to be zero), and C , H , N , O , P , and S represent stoichiometric numbers of each respective element. Molecular formulas were also assigned to major biochemical compound classes (i.e., amino sugar, carbohydrate, condensed hydrocarbon, lignin, lipid, protein, tannin, unsaturated hydrocarbon, and other) following Kim et al. (2003). We used presence/absence data to compare the relative abundances of compound classes between redox treatments.

Results

Gas fluxes

We used ^{13}C - CO_2 abundance to partition total CO_2 production between litter- and SOM-derived pools and found distinct responses to our 44-day redox

manipulation (Fig. 1a, b). Overall, the length of oxic headspace exposure was positively correlated with cumulative CO_2 produced from SOM ($r = 0.89$, $P < 0.001$, $n = 20$), but not CO_2 produced from litter ($r = -0.35$, $P = 0.14$, $n = 20$). Cumulative SOM-derived CO_2 fluxes were lowest in the static anoxic treatment, intermediate in the fluctuating treatments, and highest in the static oxic treatment (Tukey's tests: $P_s < 0.05$); soil-derived CO_2 from the static anoxic treatment was only $65 \pm 3\%$ (mean \pm standard error unless otherwise noted) of the cumulative flux measured in the static oxic treatment (Tukey's test: $P < 0.001$).

In contrast, cumulative CO_2 production derived from the decomposition of added plant litter was highest in the static anoxic treatment, and significantly greater than in the two fluctuating treatments by at least $19 \pm 6\%$ (Tukey's tests: $P_s < 0.05$, Fig. 1a). The static oxic litter-derived CO_2 flux, while higher than the high frequency soil flux, was not significantly different from the low frequency or static anoxic treatment (Fig. 1a). Across all treatments, at least $35 \pm 1\%$ of added litter C was lost via CO_2 . The combined litter- plus SOM-derived CO_2 (i.e., total CO_2) production was highest in the static oxic

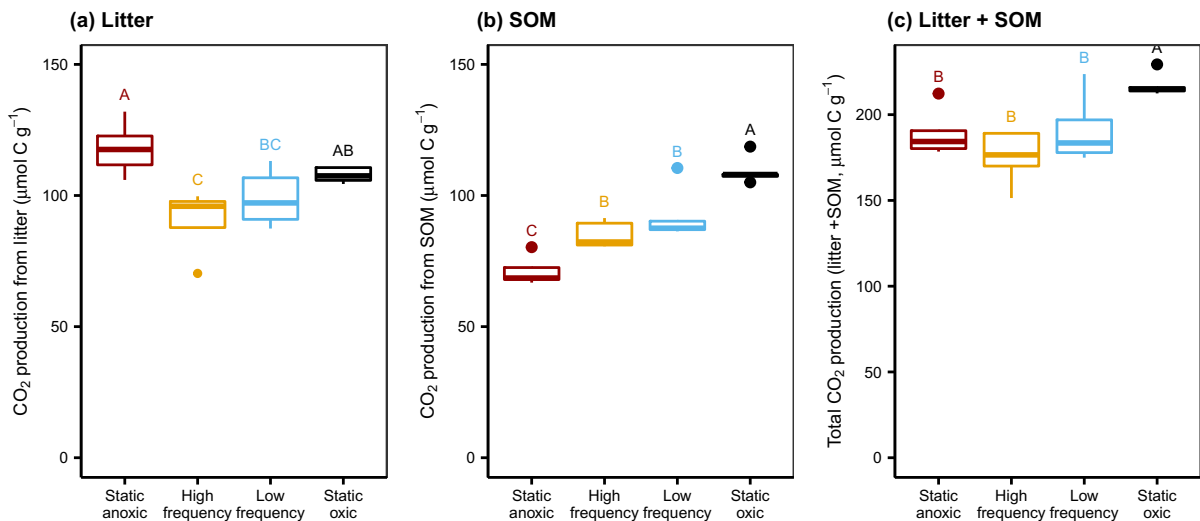


Fig. 1 Effects of four redox treatments on cumulative CO_2 production derived from litter (a), soil organic matter (SOM; b), and litter plus SOM (c) for a 44-day redox incubation of tropical soils from the Luquillo Experimental Forest, Puerto Rico. CO_2 flux was partitioned between litter and SOM using ^{13}C - CO_2 abundance and an isotopic mixing model. Boxplot whiskers represent 1.5 times the interquartile range of the data. Letters not in common indicate significant difference at $\alpha = 0.05$ level

(Tukey's tests). From left to right, redox treatments had increased exposure to headspace oxygen, $n = 5$ per treatment. Static anoxic and oxic conditions were maintained by flushing incubation headspace with N_2 or air, respectively; "high" and "low" frequency fluctuation incubations oscillated between redox states (4 days oxic/4 days anoxic (high frequency), 8 days oxic/4 days anoxic (low frequency)). Note that the scale of CO_2 production is different in panel (c)

treatment (Tukey's test: $P < 0.001$), and not statistically different amongst static anoxic, high frequency, and low frequency treatments (Fig. 1c).

Litter-derived CO_2 fluxes responded distinctly to redox treatments over time. During the early part of the experiment, fluxes were significantly higher in the static anoxic treatment relative to other treatments (Fig. 2; $P_s < 0.05$ for days 5 and 8; $P_s < 0.10$ for days 12 and 16). After three weeks of incubation, litter CO_2 production had significantly declined in all treatments, and by the final two sampling timepoints (days 41 and 44), litter CO_2 production was $13 \pm 1\%$ of initial values (i.e., the first two timepoints), and significantly lower in the static anoxic treatment (Tukey's tests: $P_s < 0.05$, Fig. 2).

Unlike litter decomposition, the decomposition of SOM did not change during the 44-day incubation, except in the static anoxic treatment, where rates decreased with time ($r = -0.66$, $P < 0.001$, $n = 60$) (Fig. 2) and were significantly lower than static oxic soils after the third week (Tukey's tests: $P_s < 0.05$). Compared to the two fluctuating redox treatments, static anoxic soils also had lower SOM-derived CO_2

production on days 28, 36, 41, and 44 (Tukey's tests: $P_s < 0.05$).

Both litter- and SOM-derived CO_2 fluxes responded to the short-term redox shifts imposed by our two fluctuating treatments (Fig. 3). SOM-derived CO_2 production was $29 \pm 12\%$ and $32 \pm 15\%$ lower when measured at the end of an anoxic period versus the end of an oxic period in the high-frequency and low-frequency treatments, respectively ($P_s < 0.05$). After accounting for the general decreasing trend with time (which explained over 65% of the variability), average litter CO_2 production was $36 \pm 12\%$ lower when measured following an anoxic period compared to an oxic period in the high-frequency treatment ($P < 0.05$). A similar trend was also found in the low-frequency treatment, although not statistically significant at the 95% level ($P = 0.13$).

Modeling total CO_2 fluxes

We fit the total CO_2 flux (i.e., irrespective of isotopic partitioning) to a two-pool model that characterizes decomposition using first-order kinetics of two soil C pools with distinct decomposition rates. We found that

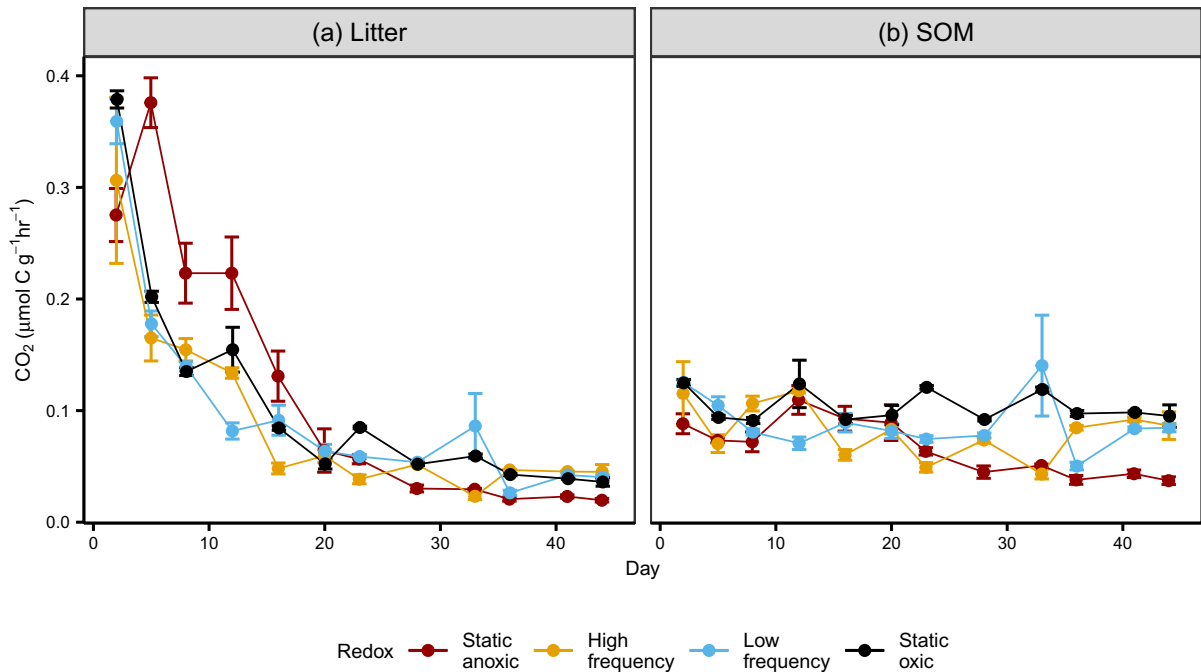


Fig. 2 Effects of four redox treatments on the instantaneous production rate of CO_2 derived from ^{13}C -litter (a) and soil organic matter (SOM, b) in a 44-day incubation study of tropical

soils from the Luquillo Experimental Forest, Puerto Rico. Error bars indicate standard errors of the means. $n = 5$ per timepoint and treatment

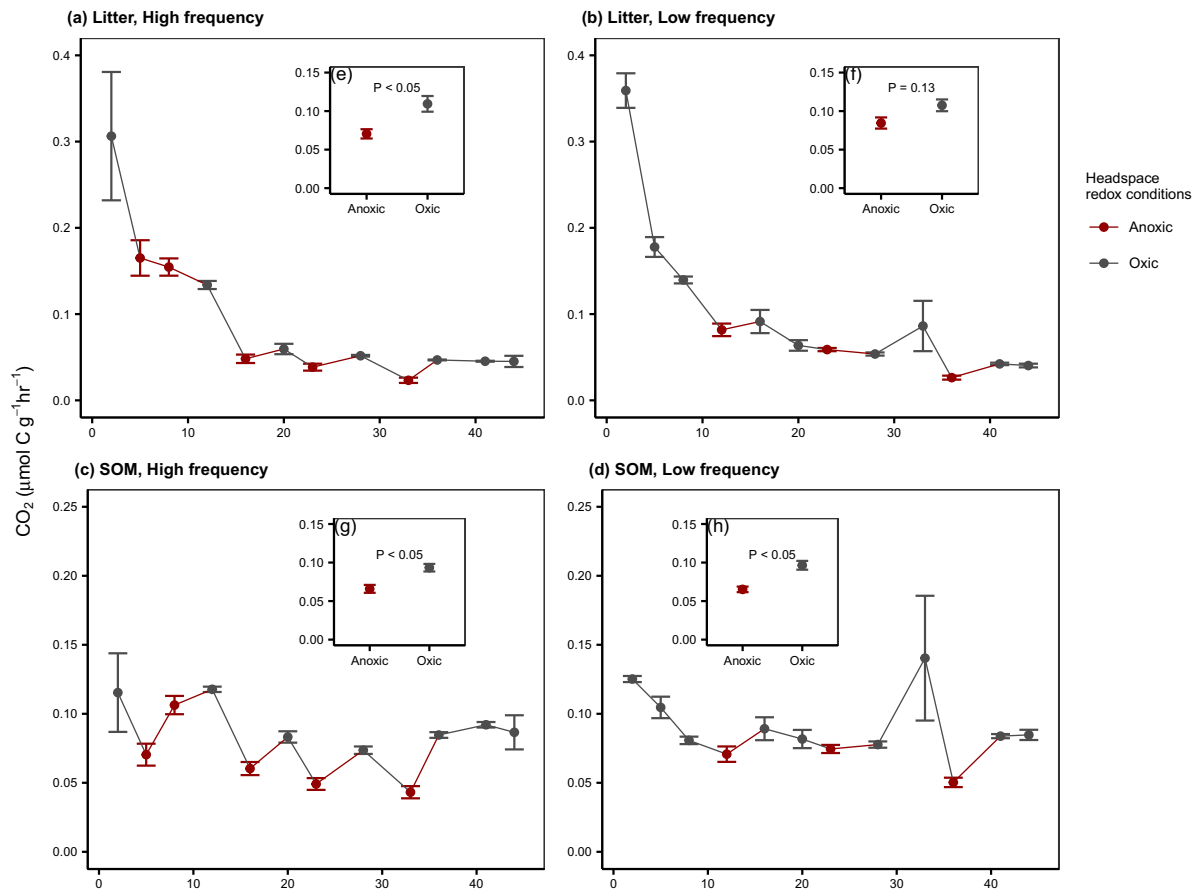


Fig. 3 Effects of headspace redox conditions (anoxic vs. oxic) on CO₂ production from litter (**a** and **b**) and soil organic matter (SOM, **c** and **d**) in high-frequency (**a** and **c**) and low-frequency (**b** and **d**) redox oscillation treatments during a 44-day incubation study. Error bars indicate standard errors of means. $n = 5$ per timepoint and treatment. Insets compare the means and

standard errors of CO₂ production under anoxic vs. oxic headspace with P values. Litter CO₂ production in the inset figures have been adjusted against their decreasing trend over time, which was modeled as a quadratic polynomial function. See Methods for details of statistical analyses. Note that the scale of CO₂ production was different between litter and SOM

redox treatments affected the pool sizes and the rate constant of one pool (Fig. 4). The size of the fast-cycling pool (determined by coefficient γ), was the primary contributor to initial CO₂ fluxes and was substantially larger in the static anoxic treatment relative to the other treatments (ANOVA: $P < 0.001$). The rate constant of the slow-cycling pool (k_2 , thought to cycle on the order of years; Fig. 4c) was the lowest in the static anoxic treatment (ANOVA: $P < 0.001$). However, rate constants of the fast pool (k_1 , thought to cycle on the order of days; Fig. 4b) were highly variable and differences with redox were not statistically significant.

Chemistry of water-extractable organic matter

Redox patterns influenced the chemical composition of water-extractable OM according to NMDS and PERMANOVA analyses ($P < 0.05$; Fig. 5). Differences between the static anoxic treatment and other treatments were most distinct on day 20, at the end of the phase of elevated litter-derived ¹³CO₂ fluxes. We also observed redox effects on compound chemistry via NOSC values (Fig. 6). On day 20, the mean NOSC value of water-extractable OM was higher in the static anoxic than the static oxic treatment (Tukey's test: $P < 0.05$) and trended higher than the low-frequency treatment (Tukey's test: $P = 0.12$); there were no

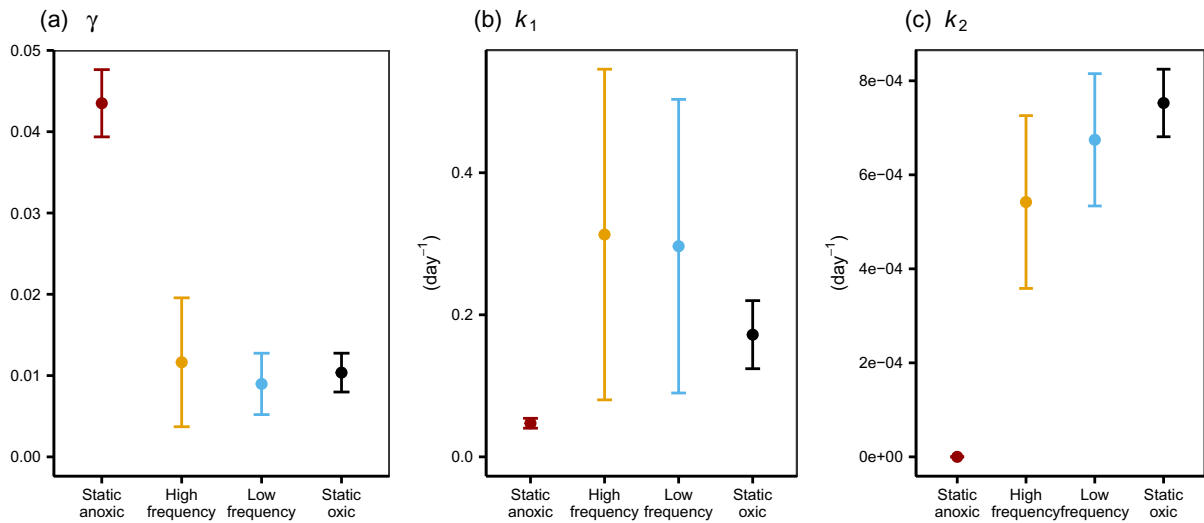


Fig. 4 Effects of four redox treatments on coefficient estimates of a two-pool decomposition model applied to CO₂ fluxes from a tropical redox incubation study. Modeled coefficients include: **a** γ , **b** k_1 and **c** k_2 , where γ is the coefficient that regulates initial C partitioning into fast- and slow-cycling pools, and k_1 and k_2

are decomposition constants for the fast- and slow-cycling organic carbon pools, respectively. Error bars indicate standard deviations of the coefficient distributions obtained through Bayesian optimization

mean NOSC differences with treatment on day 36 or 44.

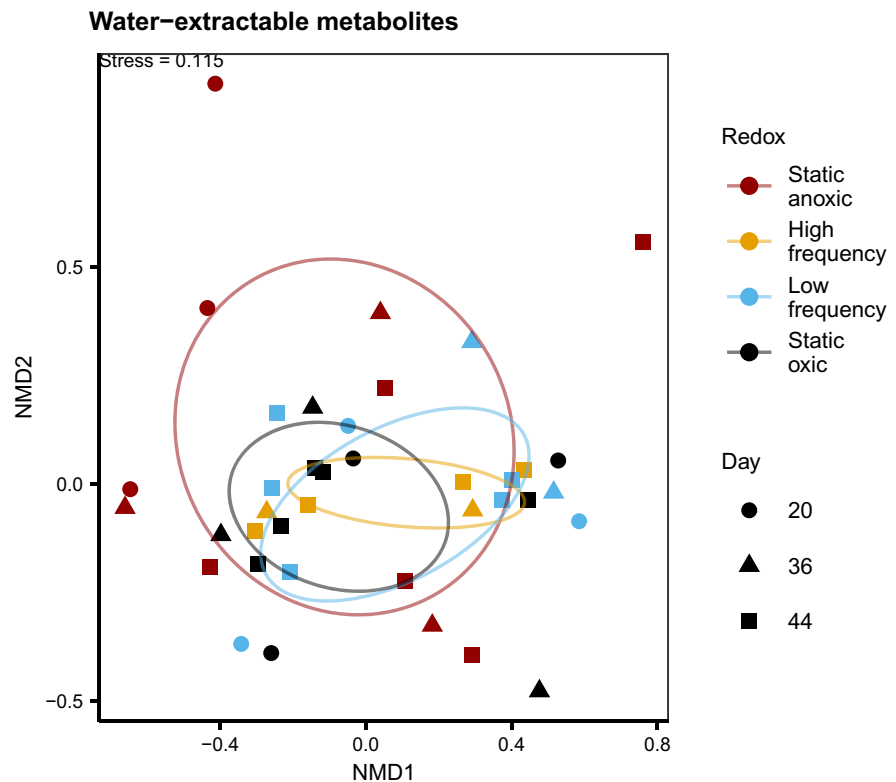
Redox effects were also apparent when we examined the relative abundances of specific compound classes (Fig. S3). On day 20, carbohydrate- and protein-like compounds were enriched in the static anoxic treatment compared to other treatments (Tukey's tests: $P_s < 0.05$). In the static anoxic soils, amino sugar-like compounds were also more abundant than in the static oxic treatment (Tukey's test: $P < 0.05$) and marginally higher than the low-frequency treatment (Tukey's test: $P < 0.10$). The relative abundance of lignin-like compounds trended lower in the static anoxic than the other treatments (Tukey's tests: $P_s < 0.10$). In contrast, redox treatments did not affect abundance of any compound class on days 36 (data not shown) or 44. We note these redox effects on compound chemistry were not driven by wholesale changes in total DOC concentrations (Fig. S4), which were higher in the static anoxic treatment on both day 20 (Tukey's tests: $P_s < 0.05$) and day 44 (Tukey's tests: $P_s < 0.01$).

Discussion

Although we predicted that low O₂ concentrations would decrease both litter and SOM decomposition, the isotopic partitioning in our tracer study revealed distinct effects of redox manipulations on the decomposition of plant litter and SOM. Surprisingly, litter decomposition rates were the highest under static anoxic conditions early in our experiment, suggesting that soil anaerobes were able to effectively use some of the added litter-derived compounds. In the static oxic and fluctuating soils, litter CO₂ fluxes were also high immediately after the litter addition, but gradually declined over time. In contrast, litter CO₂ fluxes in the static anoxic soils did not peak until 5 days after the litter addition and remained higher than other treatments until day 20. These patterns suggest static anoxic conditions promoted decomposition of litter-derived compounds over a sustained period of time. Microbially-available litter compounds were nearly exhausted by the end of the 44-day experiment, when the litter decomposition rates in all treatments were very low (and lowest in static anoxic soils).

Redox effects on labile compound decomposition were also apparent in the FTICR-MS results. Halfway through our study, the mean NOSC value of water-extractable OM was higher in the static anoxic soils

Fig. 5 Non-metric multidimensional scaling (NMDS) plot comparing the composition of water-extractable organic matter among redox treatments and among sampling days. Data were derived from FTICR-MS analysis. The ellipse indicates the standard deviation of each redox treatment. High frequency treatment from day 20 and two other samples were not included due to low number of peaks (< 200). See Materials and Methods for details



than other treatments. Day 20 also marked a point when amino sugar-, carbohydrate-, and protein-like compounds were more enriched in the static anoxic soils relative to static oxic soils. By the end of the experiment, however, DOC chemistry was no longer different between the static anoxic treatment and other treatments. Coinciding with temporal changes in compound chemistry, declines in CO_2 production was observed only in the static anoxic treatment, even though DOC concentration was consistently higher in the static anoxic treatment than in other treatments. These results suggest that only a subset of DOC was used as substrates by anaerobic microbes. More specifically, anaerobes preferentially used soluble compounds with relatively high NOSC values and/or in the forms of amino sugars, carbohydrates, and proteins, which is consistent with thermodynamic constraints of anaerobic metabolism (Jin and Bethke 2003; LaRowe and Van Cappellen 2011; Boye et al. 2017). Over the second half of the experiment, depletion of thermodynamically favorable compounds resulted in the declines in CO_2 fluxes, while the non-labile compounds accumulated by the end of the

experiment. We also suspect that similar preferential decomposition of compounds had occurred early in the experiment. Together, the gas flux and soil chemistry data indicate that high NOSC labile compounds were derived from litter and preferentially degraded by anaerobic decomposers in the anoxic treatment. Labile compounds can be readily used via fermentation and substrate-level phosphorylation, while O_2 limitation inhibits use of peroxidases and oxidases and thus depolymerization of complex compounds such as lignin and tannin (Reineke 2001; Sinsabaugh 2010). Rapid anoxic litter decomposition occurred only in the early phase of the incubation; we expect similar phenomena may occur under field conditions due to frequent additions of fresh litter and root exudate inputs.

In contrast to litter decomposition, native SOM decomposition was clearly limited by anoxic conditions. The SOM likely contained a lower proportion of the intermediate-high NOSC easily degradable compounds preferred by microbial decomposers. Our results indicate that the source of organic matter (litter vs. SOM) influences the rate at which decomposition

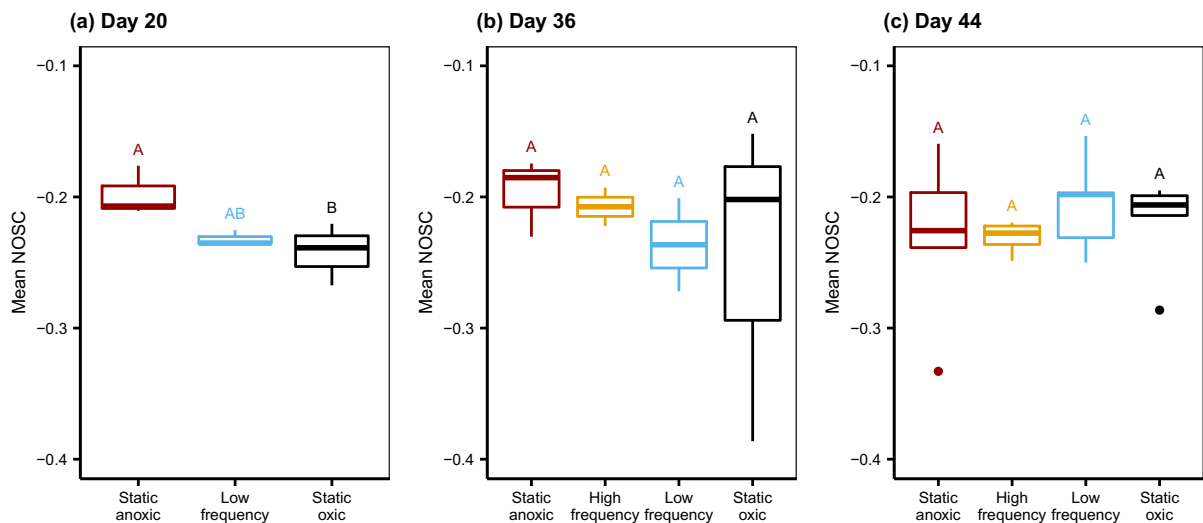


Fig. 6 The mean nominal oxidation state of carbon (NOSC) value of water-extractable organic matter from a tropical soil incubated under four redox regimes collected on **a** day 20, **b** day 36, and **c** day 44 of the experiment. Data were derived from FTICR-MS analysis. Boxplot whiskers represent 1.5 times the interquartile range of data. Means with letters not in common are

significantly different at $\alpha = 0.05$ level (Tukey's tests). On days 20 and 36, $n = 3$ per treatment. On day 44, $n = 5$ per treatment. High frequency treatment from day 20 and two other samples were not included due to low number of peaks (< 200). See Materials and Methods for details

processes are impacted by redox conditions. In this humid tropical forest soil, aerobic and anaerobic heterotrophs were equally effective at degrading labile substrates released from fresh plant litter, while aerobic decomposers were more effective in breaking down the potentially refractory compounds found in SOM, as expected based on the role of O_2 in oxidative activity. Similar effects of substrate energetic availability have been reported in marine sediments and wetlands (Hulthe et al. 1998; Kristensen and Holmer 2001), but not in upland soils. In our experiment, anoxic SOM decomposition rates were approximately 65% of those under oxic conditions (i.e., $r_{\text{oxygen}} = 65\%$), higher than the r_{oxygen} values prescribed in numerical models (2%–40%; reviewed by Keiluweit et al. 2016). This indicates that the microbial community in this soil may be particularly adapted to anoxic conditions (Pett-Ridge and Firestone 2005; DeAngelis et al. 2010; Pett-Ridge et al. 2013), likely because of the system's characteristic redox variability (Silver et al. 1999; Liptzin and Silver 2015).

Iron reduction likely played a key role in sustaining high decomposition rates under low redox conditions. High abundance and activity of Fe-reducing bacteria have been commonly observed in soils from this ecosystem (DeAngelis et al. 2010; Dubinsky et al.

2010). Using unlabeled litter additions and similar redox regimes, a companion study (Bhattacharyya et al. 2018) observed significant Fe reduction and higher DOC levels under static anoxic conditions, likely because Fe reduction triggered the dissolution of organo-Fe complexes and mobilization of OM (Pan et al. 2016; Huang et al. 2020). By weakening mineral protection of OM, Fe reduction could have helped to sustain the level of relatively oxidized compounds that we observed in the dissolved fraction; decomposition of these compounds could be readily coupled with anaerobic metabolisms, including Fe reduction (Keiluweit et al. 2016), leading to the high rates of CO_2 production we observed under static anoxic conditions.

Results from our modeling analysis further suggest that different C pools had contrasting responses to changes in O_2 availability; the rate constant of the slow-cycling pool was the lowest under anoxic headspace, while that of the fast-cycling pool was not. As noted above, the partitioning of total C between fast-cycling and slow-cycling pools was independent of that between litter and SOM. Thus, our modeling and isotopic evidence independently suggest that substrate source differentially affects redox sensitivity of SOM decomposition. The

modeling analysis also indicates the fast-cycling pool was larger in the static anoxic treatment than in other treatments, consistent with the observation that a high litter decomposition rate was maintained for an extended period time under anoxic conditions. A larger fast-cycling C pool is also consistent with the higher DOC concentrations measured here (and in Bhattacharyya et al. 2018) under anoxic conditions. Together, our results highlight that different soils and soil C pools may need to be reflected with distinct r_{oxygen} values in biogeochemical models.

Periodic anoxic events consistently decreased CO_2 production from litter and SOM in our fluctuating treatments, suggesting that even brief exposure to anoxia inhibited some SOM decomposition. These patterns contrast with our finding that static anoxic conditions increased litter decomposition relative to static oxic conditions, at least early in our incubation. This implies that the duration and frequency of low redox events may be critical to how their impacts regulate decomposition processes. Redox oscillation likely promotes facultative microbial communities and ‘tolerant’ obligate taxa (Pett-Ridge and Firestone 2005). These microbes might have lower growth potential compared to strictly aerobic/anaerobic taxa, as predicted by the recently described trade-off between stress tolerance and growth performance (Maynard et al. 2019). Recent studies also indicate that Fe(II) oxidation, which is typically rapid in fluctuating redox environments, can preferentially protect aromatic lignin compounds (from plant litter) from decomposition (Hall et al. 2016b; Wang et al. 2017). These co-occurring microbial and geochemical mechanisms need to be better explored, since frequent redox oscillation is increasingly being recognized in upland ecosystems (Keiluweit et al. 2016).

Soil redox dynamics are highly sensitive to ongoing shifts in climate, especially in the forms of extreme weather events (e.g. drought, O’Connell et al. 2018 and hurricanes, Hogan et al. 2020); our results suggest that the source of organic matter is key to predicting how decomposition processes respond to climate changes that alter a system’s typical redox oscillation pattern. Extended drought causes prolonged soil aeration (Wood et al. 2013) and in our system has been shown to affect the composition of dissolved and soil-associated carbon pools (Bouskill et al. 2016), likely via increased aerobic decomposition of relatively refractory compounds. In contrast, our results

indicate that decomposition of plant-derived, labile organic matter may be less affected by the changes in redox conditions associated with climate change. Thus, we recommend that decomposition models need to better reflect the extent of redox sensitivity (e.g., r_{oxygen}) for different soil C pools.

Conclusion

We measured distinct responses of litter and SOM decomposition to different redox conditions in a humid tropical forest soil. Litter decomposition rates under static anoxic conditions were surprisingly high during the initial weeks following litter additions, likely maintained by the decomposition of compounds with higher NOSC values. In contrast, O_2 availability limited decomposition of pre-existing SOM in anoxic and fluctuating redox soils. Static anoxic soils maintained 65% of the SOM decomposition rate measured in static oxic soils, indicating that anaerobic heterotrophs in this humid tropical soil are surprisingly effective at degrading SOM. Our results indicate that the source of soil substrates influences how redox conditions affect belowground decomposition processes and is an important consideration for numerical models of greenhouse gas fluxes from tropical forests.

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Author contributions ANC and JPR designed the incubation experiment; YL performed the gas analysis with help from ANC, JPR and AB; YL conducted modeling analysis; MMT performed the FTICR-MS analysis; YL analyzed the FTICR-MS data with help from ND, AMT, and MMT; JPR, WLS and PSN provided intellectual expertise; YL led the manuscript development with contribution from all other coauthors; JPR and WLS provided funding for experimental set-up and salary support.

Data availability Data from this study have been made available via the Luquillo CZO and Hydroshare (<http://www.hydroshare.org/resource/450692765ab444e390f40d896f1b1522>).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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