

Research



Cite this article: Chapman SK, Hayes MA, Kelly B, Langley JA. 2019 Exploring the oxygen sensitivity of wetland soil carbon mineralization. *Biol. Lett.* **15**: 20180407. <http://dx.doi.org/10.1098/rsbl.2018.0407>

Received: 12 June 2018

Accepted: 11 December 2018

Subject Areas:

ecology

Keywords:

carbon mineralization, oxygen, blue carbon, oxic : anoxic ratios, coastal wetland

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Electronic supplementary material is available online at <http://dx.doi.org/10.6084/m9.figshare.c.4341131>.

Exploring the oxygen sensitivity of wetland soil carbon mineralization

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Soil oxygen availability may influence blue carbon, which is carbon stored in coastal wetlands, by controlling the decomposition of soil organic matter. We are beginning to quantify soil oxygen availability in wetlands, but we lack a precise understanding of how oxygen controls soil carbon dynamics. In this paper, we synthesize existing data from oxic and anoxic wetland soil incubations to determine how oxygen controls carbon mineralization. We define the oxygen sensitivity of carbon mineralization as the ratio of carbon mineralization rate in oxic soil to this rate in anoxic soil, such that higher values of this ratio indicate greater sensitivity of carbon mineralization to oxygen. The estimates of oxygen sensitivity we derived from existing literature show a wide range of ratios, from 0.8 to 33, across wetlands. We then report oxygen sensitivities from an experimental mesocosm we developed to manipulate soil oxygen status in realistic soils. The variation in oxygen sensitivity we uncover from this systematic review and experiment indicates that Earth system models may misrepresent the oxygen sensitivity of carbon mineralization, and how it varies with context, in wetland soils. We suggest that altered soil oxygen availability could be an important driver of future blue carbon storage in coastal wetlands.

1. Introduction

Owing to high productivity and low organic matter (OM) decomposition in saturated soils, coastal wetlands, the marshes and mangroves that line the world's coasts, store inordinate quantities of organic carbon (C) in the biosphere [1,2]. This C sequestered in mangroves and marshes, along with seagrass ecosystems, is often termed 'blue carbon' and represents a long-term C sink. Recent studies have provided reliable estimates of coastal soil organic C [3,4] and previous work has helped clarify the mechanisms driving soil C storage in coastal wetlands, including priming [5], disturbance [6] and eutrophication [7]. Despite these advances, future coastal wetland C storage and greenhouse gas efflux [8] remain difficult to predict.

High stocks of wetland soil C result largely from an imbalance of below-ground productivity and OM decomposition and from the trapping of sediment particles [9]. To date, studies in coastal wetlands have investigated the influences of salinity [10], elevated carbon dioxide (CO₂) [11], nutrient availability [12], plant type [13] and water level [14] on wetland soil C dynamics. Redox conditions can also influence OM decomposition [15] but, at low oxygen (O₂) conditions and where tides can introduce molecular oxygen, such as in temperate and tropical coastal wetlands, redox may be a less important driver of microbial C processing than O₂ availability. Oxygen availability may be an important factor influencing C mineralization in freshwater wetlands [16] but has received less experimental attention in coastal wetlands [6,11].

Conventional wisdom holds that scarcity of O_2 in wetland soils explains the inordinate C storage per area of wetlands. In saturated soils, water fills the spaces between soil particles, so that O_2 must diffuse through water, which is 8400 times slower than through air at 25°C. As a result, microbial metabolism and abiotic processes may consume O_2 more quickly than it is replenished through diffusion. Because aerobic respiration is thermodynamically more efficient per molecule of the substrate than anaerobic respiration using alternative terminal electron acceptors, deprivation of O_2 in soils is thought to slow microbial activity and thus OM decomposition, promoting soil C accumulation [17]. Recent studies using planar optodes have shown that sediment $[CO_2]$ increases around oxygenated root surfaces [18], indicating that decomposition is stimulated to some degree.

If O_2 drives OM decomposition, any change in O_2 availability may have dramatic consequences for wetland soil C storage (figure 1). Our understanding of microbial responses to O_2 changes could be advanced by *in situ* molecular examinations of coastal wetland microbial communities [19] and/or by O_2 manipulation experiments. We can use wetland incubation studies that manipulate oxygen to draw generalities about oxygen sensitivity, defined herein as the factor by which C mineralization in fully oxic soil differs from fully anoxic soil. However, few studies have manipulated O_2 availability in a way that allows extrapolation to real soil conditions. Nearly all incubations apply O_2 treatments by oxygenating the headspace of a sealed container enclosing either intact soil monoliths or mixed slurries. In the case of intact soils, the headspace O_2 in oxic treatments does not penetrate soil fully (electronic supplementary material, figure S1). In the case of slurries, the O_2 treatment is applied homogeneously, but soil microstructure is disturbed. Agitating soils in slurries increases respiration rates several fold because it disrupts gradients rendering resources unrealistically available [20]. Both approaches may misrepresent the effects of oxygenation in actual soils; thus, intact soils and consistent treatment application are required to represent microsite processes accurately.

Understanding blue C dynamics under future environmental conditions, which will include perturbations that alter O_2 availability such as increased droughts, higher sea levels and shifting dominant wetland plant species, requires a more nuanced understanding of how oxygen availability drives C mineralization in coastal wetlands. To accurately project future C emissions from wetlands, global climate models currently make assumptions about the O_2 sensitivity of C mineralization and use a scalar to slow C mineralization in anoxic soils, like those of wetlands [21]. In this paper, we first aim to summarize the current knowledge on the oxygen sensitivity of C mineralization (both CO_2 and CH_4) from wetland soil incubation data. Second, we describe and present data from a flow-through mesocosm system developed to manipulate O_2 availability independently from other variables in realistic soils. Finally, we discuss global changes that could alter soil oxygen availability and discuss their implications for blue C assessments and Earth system model parametrization (figure 1).

2. Material and methods

(a) Systematic review of oxic : anoxic ratios

Briefly, we performed a Web of Science literature search to find studies that investigated CO_2 and CH_4 respiration in wetland

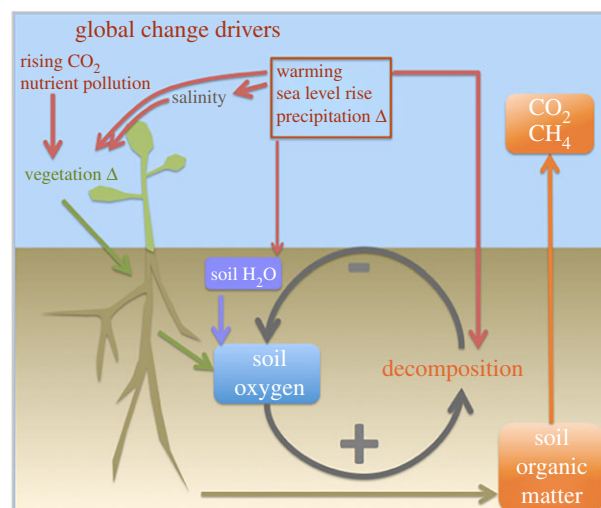


Figure 1. Mechanisms by which soil oxygen can impact soil carbon dynamics (orange text and boxes). Red and green text and arrows indicate the global change drivers that can indirectly alter soil oxygen availability.

soils using both oxic and anoxic incubation conditions (see electronic supplementary material methods for details and statistical analyses). We calculated oxic to anoxic CO_2 and CH_4 respiration ratios (heretofore termed 'O : A ratios') for each study by dividing the rate of oxic respiration by the rate of anoxic respiration (electronic supplementary material, table S1). We report the error as standard error unless otherwise noted.

(b) Flow-through mesocosms

We took five intact soil monoliths from 0 to 30 cm depth including roots from a brackish, tidal wetland, Kirkpatrick Marsh near Edgewater, MD (described in [13]). We divided the 10–15 cm depth of each monolith laterally for paired oxic or anoxic mesocosms (resulting soil profiles were 5 cm diameter by 5 cm depth). We designed flow-through mesocosms (pictured in figure 2, detailed methods in electronic supplementary material) to recirculate porewater that was either oxygenated or deoxygenated, yielding a consistent, verifiable and homogeneous amount of O_2 in intact soil profiles (electronic supplementary material, methods). We assessed O_2 treatments with a four-channel oxygen meter system (FirestingO2, Pyroscience, Aachen, Germany, electronic supplementary material, figure S1) throughout the soil profile. Approximately twice weekly for six weeks, we sealed the mesocosms and immediately measured respiration as headspace accumulation of CO_2 by manually taking five headspace gas samples over 3 h. Gas samples were stored in syringes and analysed after sampling by injecting on an infrared gas analyser (Li-7000, Li-cor, Lincoln, NE) configured for discrete sample injection with a six-port valve (Valco Instruments). Previous work has shown that CH_4 emissions from these brackish soils represent a negligibly small fraction of total C lost from decomposition.

3. Results

(a) Literature-derived oxic : anoxic ratios of carbon mineralization

Across all wetland types CO_2 O : A ratios ranged from as low as 0.8 in a bog system up to as high as 33.2 in a tropical wetland system (electronic supplementary material, table S1). Across all wetland types, the mean O : A ratio was 7.06 ± 1.21 (table 1). CO_2 O : A ratios varied significantly across wetland types ($F_{5,27} = 18.40$, $p < 0.001$) with the most significant

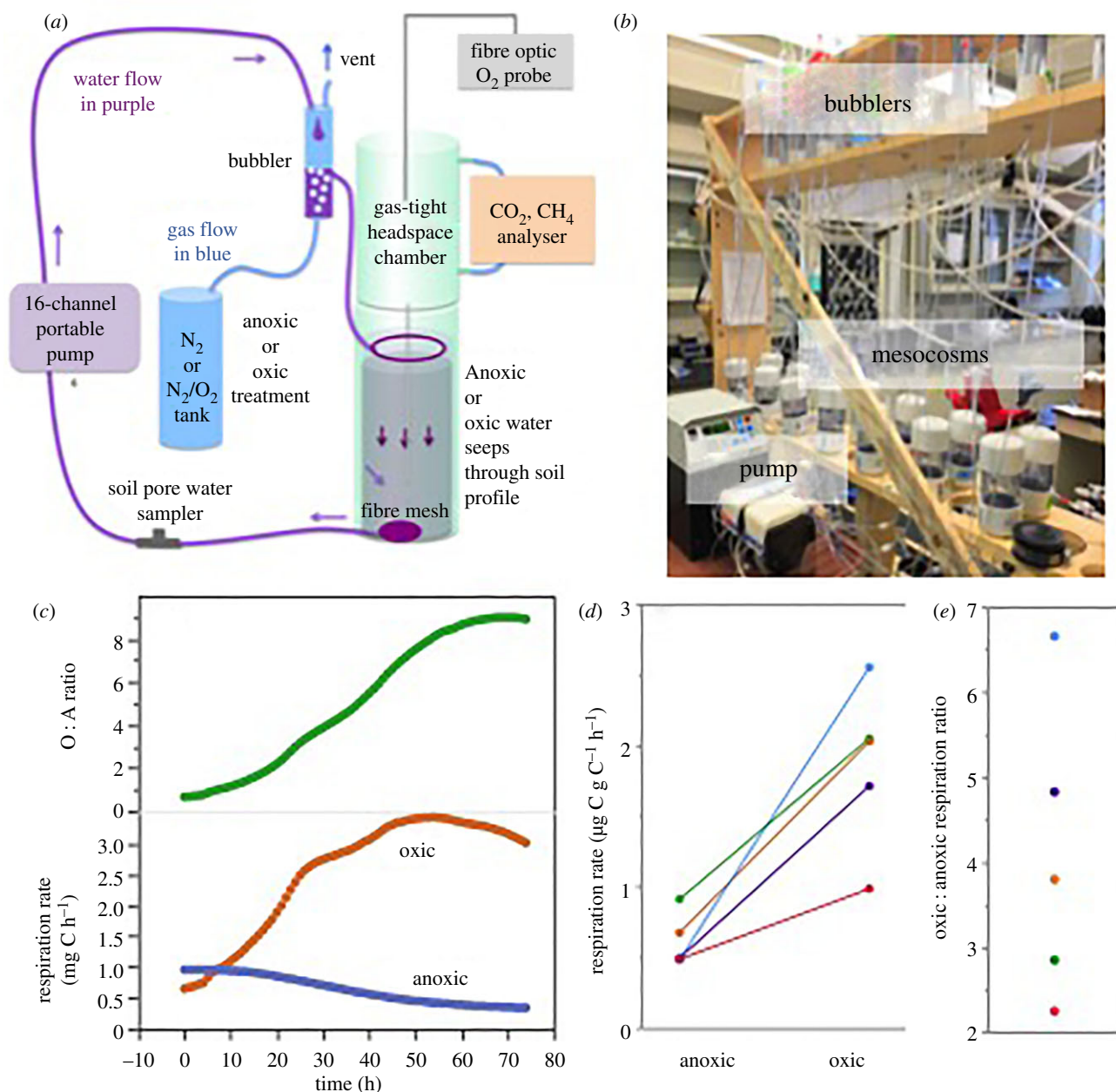


Figure 2. Schematic (a) and image (b) of flow-through mesocosm system. An example of continuous respiration measurements (c) from a pair of soils, one oxidized at time 0 and one remaining anoxic. The six-week mean respiration rates (d) from five soil pairs, and the corresponding ratio of oxitic-to-anoxic respiration (e) for each pair (varied by colour).

differences being between tropical wetlands and all other wetland types ($p < 0.05$) and between fen and bog wetland systems ($p < 0.05$). There were no differences in O : A ratios between other wetland types ($p > 0.05$). Mean O : A ratios were highest in tropical wetland systems with mean O : A ratios of 15.96 and were lowest in moors and pocosins with O : A ratios of 2.86 and 2.15, respectively (table 1). Total C mineralization ratio, including CO₂ and CH₄, ranged from as low as 4.32 within a bog system up to 13.4 within a tropical wetland system, with a mean O : A respiration ratio of 8.17.

There was also a significant difference in O : A ratios across studies ($F_{10,27} = 6.11$, $p < 0.001$) suggesting some variability in O : A ratios not only between individual studies and wetland types but also within the same wetland types across studies. For example, one bog had an O : A ratio of 7.7 while a bog in another study had a much lower ratio of 0.8 (electronic supplementary material, table S1).

(b) Experimental oxygen manipulation mesocosm O : A ratios

The oxygen treatments were consistent throughout the soil profile. Oxitic mesocosms averaged 9.3 ± 1.2 mg O₂ l⁻¹ porewater (mean \pm s.d. across mesocosms). [O₂] generally decreased slightly with depth as O₂ was consumed but never below 8.2 mg O₂ l⁻¹. Anoxic mesocosms averaged 0.02 ± 0.40 mg O₂ l⁻¹ and were not significantly different from 0, though we did see evidence of O₂ diffusion through our porewater delivery tubing. Over six weeks, the O : A respiration ratio ranged from 0.7 to 13.9 across five pairs of mesocosms. The ratio varied through time but did not exhibit consistent directional change even though respiration rate tended to decline (electronic supplementary material, table S2). The global mean across soils and time was 4.1 (s.d. = 2.99). The mean ratio for five pairs each averaged across 12 measurements over six

Table 1. Mean and standard errors for the CO₂ and CO₂ + CH₄ (total C respiration including CO₂ and CH₄). Oxidation:anoxia ratios derived from the systematic review. The oxidation to anoxia (O:A) CO₂ and CH₄ ratios on which these means are based were calculated for each study by dividing the rate of oxic carbon respiration by the rate of anoxic respiration.

wetland type	mean CO ₂ O : A ratio	mean CO ₂ + CH ₄ ratio
bog	3.8 ± 3.67 (n = 12)	4.32 ± 1.82 (n = 4)
fen	7.0 ± 8.23 (n = 15)	6.48 ± 7.55 (n = 13)
moor	2.86 ± 1.26 (n = 3)	n.a.
swamp	3.8 ± 1.1 (n = 4)	4.95 ± 0.69 (n = 2)
tropical wetland	15.96 ± 10.3 (n = 9)	13.4 ± 9.4 (n = 9)
pocosin	2.15 ± 0.65 (n = 2)	n.a.
total mean across studies	7.06 ± 1.21	8.17 ± 11.62

weeks was 4.1 (s.d. = 1.7, s.e. = 0.8). The average temporal error within a soil pair was 2.4 (s.d. through time).

4. Discussion

In our literature-based examination of how O₂ availability influences C mineralization, we found that O:A ratios varied widely from 2.15 to 15.95, with tropical wetlands seeming to show more sensitivity of C mineralization to O₂ availability than other ecosystems (higher O:A ratios). Using our experimental flow-through mesocosms, we found a mean CO₂ O:A ratio of 4.1 but this value differed among soils that were taken from different locations.

Our systematic review of the literature suggests that O₂ may have a larger effect on total C respiration rate in wetlands where other factors (soil C quality, nutrient availability, low temperature) are less limiting to decomposition, such as tropical wetlands. Using a model and empirical data synthesis, Lovelock *et al.* [6] found that in the tidal marsh, mangrove and seagrass ecosystems CO₂ emissions were highly sensitive to sediment oxidation due to disturbance. In a review of permafrost soil incubations and O:A ratios, Schadel *et al.* [22] found that aerobic incubations released 3.4 (2.2 to 5.2) times more C than anaerobic incubations, indicating that, even in these permafrost ecosystems, O₂ can control the fate of carbon, whether it is emitted as CO₂ or CH₄. The mean O:A ratio of 4.1 we estimated from the flow-through mesocosms tended to be lower than 5.0 used by the Community Land Model [21] which cites two incubation studies that may have suffered from the artefacts noted above. The mean O:A ratio value we derived from the literature, 7.1, is 54% higher than this value. Earth system models have only recently begun to incorporate anoxia to better represent wetland processes and have acknowledged that the O:A ratios have not yet been explicitly confronted with experimental data [23]. Our experimentally derived ratio, the first reported for a coastal wetland to our knowledge, falls within the range of O:A ratios for freshwater wetlands (table 1, S1) and all of these values could be useful for future model parametrization.

Both the literature-derived O:A ratios and the O:A ratios from the flow-through mesocosms exhibit great variability. We do not know how much of this variability is biological and how much is methodological. Biotic and abiotic factors such as geomorphic setting, temperature, hydrology, C macromolecule structure [24] and plant composition have all been shown to limit soil OM decomposition. In our

mesocosms, a small amount of O₂ leakage may have caused an overestimation of respiration from anoxic mesocosms, and an underestimation of O:A ratios. Incomplete oxygenation of soil in incubation studies would lead to a similar oxygen sensitivity underestimation. All the methodological errors we identified have the effect of diminishing the O:A ratio estimate. Global models parametrize C fluxes with values from these small-scale error-prone incubation studies. Models that use O:A ratio values that are too low may be underestimating the sensitivity of blue C to increasing O₂ availability, as well as underestimating the stability of C under anoxic conditions. According to our results, this underestimation may be particularly severe for tropical wetlands, so the ratio may need to be dynamic depending on the environmental context. Future studies should focus on realistically simulating oxygen flow in wetlands, which is likely more complex than anoxic versus oxic conditions.

The O₂ scarcity that allows coastal wetlands to lock away such vast amounts of blue C is subject to dramatic future change. Global change can alter hydrology, salinity and sealevel, exposing coastal wetlands to drought-like conditions [25] and can affect changes in the diffusion of O₂ via wetland plants into the soil [11,26,27] (figure 1). Perhaps more importantly, climatic and other global changes also drive vegetation shifts in wetlands [28], which can have cascading effects on O₂-mediated C storage [29] (figure 1). For instance, the climate-driven expansion of woody mangroves into herbaceous marshes increases ecosystem C storage aboveground [30], but also may introduce more O₂ into rhizospheres [19], which could jeopardize existing soil C stocks. Assessments of blue C under global change require an understanding of oxygen sensitivity of wetland soil C mineralization under different hydrological regimes and plant functional types.

Data accessibility. The empirical data from the mesocosm experiment are available in electronic supplementary material.

Authors' contributions. S.C., B.K., J.A.L. designed the mesocosms. J.A.L. and B.K. carried out the mesocosm construction and data collection. J.A.L. and M.H. performed statistical analyses; M.H. conducted the systematic review. S.C., J.A.L. and M.H. and B.K. wrote the manuscript. All authors gave final approval for publication and agree to be accountable for all aspects of the work.

Competing interests. The authors have no competing interests

Funding. S.C., J.A.L. and M.H. were funded by the National Science Foundation DEB 1655659 while writing this article.

Acknowledgements. We would like to thank Chelsea Barreto, Tara Malanga, Libby O'Brien and Megan Foley for mesocosm experiment assistance.

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