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Journal

Biogeochemistry, 123(1-2)

ISSN

0168-2563

Authors

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Publication Date

2015-03-01

Peer reviewed

Title:

Non-linear response of carbon dioxide and methane emissions to oxygen availability in a drained Histosol

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Key Points:

- Histosol carbon gas fluxes were measured under a wide range of oxygen concentrations
- The response of carbon gas fluxes to oxygen concentration was non-linear
- Data indicate high sensitivity of Histosol carbon gas flux to low oxygen (< 2%) concentrations

Abstract:

Organic-rich wetland soils in the Histosol soil order represent the largest soil carbon (C) pool globally. Carbon accumulation in these ecosystems is largely due to oxygen (O_2) limitation of decomposition. Increased O_2 availability from wetland drainage and climate change may stimulate C decomposition overall and affect the balance of carbon dioxide (CO_2) and methane (CH_4) greenhouse gas release. Characterizing relationships, including non-linearity, between soil O_2 and C gas emissions is therefore critical to predict the partitioning and rate of C release from Histosols under greater O_2 availability. We varied gas-phase O_2 concentration from 0.03 to 20 % in incubations of a sapric Histosol and measured resulting CO_2 and CH_4 emissions. Efflux of CO_2 increased and CH_4 emissions decreased at higher O_2 concentrations, and rates were best described by log-linear model fits. The non-linear response of CO_2 and CH_4 emissions to O_2 concentration indicates that moist, C rich Histosols may be highly sensitive to increases in O_2 availability, even below concentration thresholds typically classified as anoxic.

Keywords:

Soil respiration; methane; carbon dioxide; oxygen; Histosol, drained peatland

Main Text: (2544 words)

Carbon-rich Histosols found in peatlands and other wetland ecosystems contain as much as one-third of Earth's soil carbon (C) pool (Limpens et al. 2008). Globally many Histosols have been drained for agriculture leading to large C losses and altered patterns of greenhouse gas emissions. Increased soil organic C oxidation and associated carbon dioxide (CO_2) emissions following drainage or natural drying of the soil have been documented in temperate (Schothorst 1977; Moore and Knowles 1989; Deverel and Rojstaczer 1996; Kasimir-Klemedtsson et al. 1997; Nieveen et al. 2005; Teh et al. 2011; Hatala et al. 2012), high-latitude (Jungkunst and Fiedler 2007; Silvola et al. 2009; Sulman et al. 2009), and tropical (Moore et al. 2013) peatland Histosols. Soil drying and water table drawdown in some regions under predicted climatic changes may have similar effects on Histosol C stocks and fluxes (Laiho 2006; Limpens et al. 2008).

The availability of oxygen (O_2) is a critical control on rates of Histosol C loss as it activates key oxidative enzymes necessary for extracellular breakdown of inhibitory phenolic compounds and permits energetically favorable aerobic respiration (Clymo 1984; Freeman et al. 2001; Freeman et al. 2004; Laiho 2006; Teh et al. 2011; Philben et al. 2014). Drainage of wetlands exposes Histosols to elevated O_2 (Laiho 2006), which can increase short-term rates of CO_2 emissions by two-fold or more compared to anaerobic conditions (Moore and Dalva 1993; Silvola et al. 1996; Blodau and Moore 2003; Chimner and Cooper 2003; Glatzel et al. 2004; McNicol and Silver 2014). Drainage also dramatically decreases Histosol emissions of methane (CH_4), a greenhouse gas 34 times more potent than CO_2 over a 100-year timescale (Myhre et al. 2013), by facilitating aerobic microbial methanotrophy in drained soil layers (Sundh et al. 1994; Hanson and Hanson

70 1996; Whalen 2005). Though vegetation composition, nutrient availability, substrate quality, and
71 temperature also regulate rates of soil C emissions across distinct wetland Histosols (Bridgham
72 et al. 2006), O_2 is a direct mechanistic control on both CO_2 and CH_4 emissions.
73
74 Over short timescales the release of CO_2 and CH_4 from Histosols is strongly influenced by rates
75 of aerobic microbial respiration and CH_4 consumption (methanotrophy), which are by definition
76 dependent on available O_2. However, to our knowledge, no studies have explicitly characterized
77 the kinetic response of these aerobic processes at aggregate-to-pedon scale to the wide range of
78 gas-phase O_2 concentration possible *in situ* (0-21 %). Oxygen is likely to occur at very low
79 concentrations in soil air under conditions of high biological O_2 demand and a tortuous gas-phase
80 diffusion environment (Grable and Siemer 1968; Silver et al. 1999; Teh et al. 2005; Hall et al.
81 2012), such as soils at depth in peatlands. With the exception of microaerophilic methanotrophs
82 (Hanson and Hanson 1996), we have surprisingly little understanding of how processes
83 important to Histosol C gas exchange are affected by low soil O_2 concentrations (< 1 %) that are
84 functionally equated with anoxic conditions in geochemical redox classifications (Berner 1981;
85 Scott and Morgan 1990; Chapelle et al. 1995). Most soil microcosm studies that manipulate O_2
86 concentration have imposed coarse (Teh et al. 2005) or narrow (Greenwood 1961) ranges, which
87 are aptly suited for mechanistic investigations, but cannot characterize a kinetic response
88 relevant to the wide range of potential *in situ* O_2 concentrations. Extant studies that contrast oxic
89 and anoxic conditions function as useful end-members, but are insufficient to investigate non-
90 linearity. Non-linear relationships, common in biophysical systems, and are important to identify
91 and characterize to accurately predict responses to environmental variance (Ruel and Ayres
92 1999). In the case of Histosols, non-linear effects of O_2 must be represented to accurately model

C biogeochemical processes. Indeed recent modeling work shows that improved representation of soil O_2 availability better predicts C fluxes from peatland Histosols (Fan et al. 2014).

There are both intrinsic and extrinsic factors that could lead to non-linearity between soil O_2 availability and emission of CO_2 and CH_4. Standard Michaelis-Menten enzyme kinetics that govern the intrinsic reaction rates of microbially mediated soil processes would predict a non-linear response of aerobic respiration or CH_4 consumption to O_2 concentration. Extrinsic factors, such as substrate availability (labile C or CH_4) or slow diffusive gas transport, could also lead to asymptotic relationships between O_2 consuming processes and O_2 concentration (Davidson and Janssens 2006). In this study, we test the hypothesis that the aerobic processes underlying CO_2 and CH_4 emissions from peatland soils are highly sensitive to O_2, resulting in asymptotic, non-linear relationships between C gas fluxes and O_2 concentrations. To test this hypothesis we measured the short-term responses of CO_2 and CH_4 emissions in incubations of a drained peatland Histosol to a wide range of gas-phase O_2 concentrations.

We collected approximately 6 kg of soil from the vadose zone-water table interface in a drained peatland pasture located on Sherman Island, in the Sacramento San-Joaquin Delta, CA. Similar to other Delta regions globally, the Sacramento Delta has experienced extensive land reclamation over the last 150 years (Deverel and Rojstaczer 1996). The contemporary soil profile consists of a 25 to 92 cm oxidized layer overlying a thick sapric peat horizon (Table 1) (Drexler et al. 2009). We used peat soil from 80-100 cm depth that straddles the water table and therefore has only undergone slight oxidation and is classified as a sapric Histosol (mucky peat). Soils at this depth were wet, but not saturated at the time of collection (Table 1); moisture increases seasonally to

116 saturation in summer-time due to managed water table increases. Soil CN concentration and bulk
117 density by depth are reported in Table 1 (unpublished data). Steep, persistent O_2 concentration
118 gradients with depth have been observed at the site (Figure 1). Data are averages of hourly gas-
119 phase O_2 measurements collected in March 2012 (n = 744) using calibrated galvanic cell sensors
120 (Apogee Instruments, Logan, Utah) installed at 10, 20, and 30 cm in watertight PVC cylinders
121 with a Gore-Tex seal at one end that permitted soil-chamber gas exchange (Liptzin et al. 2010).
122 The soil exhibits a consistent structure composed of fine (~mm) spherical aggregates with low
123 bulk density (Table 1), thus only gentle mixing by hand was required to homogenize slight
124 moisture differences within the sampled soil. Any stones and green plant material introduced
125 during soil collection were removed in the laboratory before approximately 200 g samples were
126 transferred to either 1 L (946 cm^3) (higher O_2 treatments) or 4 L (3,786 cm^3) sized Mason jars
127 (lower O_2 treatments). Larger jars were used for low O_2 treatments to minimize the effect of O_2
128 consumption and sample removal on headspace O_2 concentrations during the incubation. The jar
129 headspace was made anaerobic using a 2 hr pre-incubation in a glovebox and purging the
130 headspace with Ultra-High Purity (UHP) N_2 (Praxair, Richmond, CA) at 10 PSI. Flow rates and
131 timing required for removing O_2 below detectable limits were determined *a priori* using a
132 galvanic cell sensor (Apogee Instruments, Logan, Utah). Jars were then fitted with gas-tight lids
133 and incubated in the dark (i.e. in boxes) to prevent phototrophic CO_2 consumption.
134
135 Seven O_2 treatment levels (0.03, 0.1, 0.3, 1, 3, 10, 20 %; n = 4) were achieved by quantitative
136 additions of either Ultra-Zero Air (19.5-23.5 % O_2, balance N_2), or UHP O_2 (99.993 % O_2;
137 Praxair, Richmond, CA). Treatment O_2 concentrations below 0.03 % were not attempted because
138 the precision with which the residual O_2 concentration in jars after N_2 flushing was known at the

same order-of-magnitude as the lowest O_2 treatment (± 0.01 % O_2). Headspaces were mixed 10 times with a 10 ml syringe after O_2 additions and 20 ml headspace subsamples were taken immediately after mixing, and after 2, 4, and 6 h of incubation. Incubations were conducted at room temperature (21 °C) and significant pressure changes were avoided by replacing headspace after sample removal with either UHP N_2 (low O_2 treatments), 10 % O_2 in N_2 (10 % treatment), or Ultra-Zero Air (20 % treatment). Gas (CO_2 and CH_4) concentrations were determined on a Shimadzu GC-14A gas chromatograph (Shimadzu Scientific Inc., Columbia, Maryland, USA) equipped with TCD and FID detectors and calibrated with standard gas containing 997 ppm(v) CO_2 and 9.91 ppm(v) CH_4.

Fluxes were computed from the linear term of a second-order polynomial fit (CO_2 flux) or linear fit (CH_4) and accepted if fit $R^2 \geq 0.99$ (12.5 % fluxes rejected). Flux data were plotted against O_2 concentration with both linear and log-linear regressions, and fits were compared using the coefficient of determination (R^2) and the distribution of residuals as performance metrics. Direct comparison of the R^2 is a fair metric for significant relationships ($P < 0.001$) in this case because only one parameter is being estimated in both linear and log-linear fits, for $[O_2]$ and $\log_{10}[O_2]$, respectively. Quasi-Michaelis-Menten (*q*MM) parameters (maximum reaction velocity (*q*Vmax) and half saturation constants (qkM_{O2})) were estimated by normalizing fluxes to the mean flux observed at the lowest O_2 concentration treatment (0.03 %) that forced model fits through the origin. We qualify the parameters as *q*MM as they are not strict measures of single-enzyme reaction rates. Simultaneous effects of O_2 on both aerobic and anaerobic processes (e.g. CH_4 oxidation and production) and other limiting factors, such as rates of diffusive gas transport across the soil air-water boundary or C substrate availability, mean the qMM parameters should

be interpreted without mechanistic specificity. All data analysis was performed in open-source statistical software package, R (v. 2.15.2, Vienna, Austria).

Mean soil CO_2 emissions significantly increased ($P < 0.001$) with increasing O_2 concentration (Figure 2a,b; Table 2) from 180 ± 5 μg C g^{-1} d^{-1} at 0.03 % O_2 to 227 ± 16 μg C g^{-1} d^{-1} at 20 % O_2. A log-linear fit outperformed a linear model fit to all data by both metrics: log-linear R^2 was 0.49 in contrast to 0.38 for the linear model (Table 2), and the residuals more closely approximated a normal distribution (Supp. Mat. Figure 1a,b) with less skewing at lower fitted values. Crucially, the modeled y-intercept (background anaerobic respiration rate) was much lower with the log-linear fit (126 μg C g^{-1} d^{-1}) than the linear fit (186 μg C g^{-1} d^{-1}), thus the total modeled effect of oxic conditions (~20 % O_2) on respiration was thus much larger with the log-linear fit (75 % increase) compared to the linear fit (24 % increase). After normalizing data by lowest O_2 treatment we extracted a *q*Vmax for aerobic respiration of 47.3 μg C g^{-1} d^{-1} and *q*kM_{O2} of 2.2 % O_2.

Mean soil CH_4 emissions decreased ($P < 0.001$) with increasing O_2 concentration (Figure 2c, d) from 303 ± 32 ng C g^{-1} d^{-1} at 0.03 % to 77 ± 11 ng C g^{-1} d^{-1} at 20 % O_2. A log-linear model greatly outperformed a linear model fit by both metrics: log-linear R^2 was 0.70 compared to 0.40 for the linear fit (Table 2), and the residuals vs. fitted value distribution improved with the log-linear fit (Supp. Mat. Figure 1c, d). The modeled y-intercept (background CH_4 production rate) was twice as large (0.42 μg C g^{-1} d^{-1}) for the log-linear fit, than for the linear fit (0.21 μg C g^{-1} d^{-1}), and the modeled effect of 20 % O_2 was thus proportionally larger (-383 % for log-linear vs. -

257 % for linear). After normalization we extracted a *q*Vmax for aerobic methanotrophy of -0.18 μg C g^{-1} d^{-1} and a qkM_{O2} of 0.2 %.

We found that heterotrophic respiration rates increased with greater available gas-phase O_2 as would be anticipated given the favorable conditions for aerobic decomposition: namely moist, C--rich soil, not yet at steady-state with the oxidizing atmosphere (Clymo 1984; Laiho 2006; Philben et al. 2014). Importantly, we found that a log-linear model better described the relationship than a linear model and the approximated qkM_{O2} indicated a high sensitivity of aerobic respiration rates to available O_2 with 50 % of stimulated respiration occurring below 2.2 % O_2. This stands in contrast to geochemical characterizations of soil redox that often refer to soils as functionally anoxic below a 1 % gas-phase O_2 concentration (Berner 1981; Scott and Morgan 1990; Chapelle et al. 1995). Other soils, however, may display varying degrees of O_2 sensitivity where other extrinsic factors become rate limiting, such as soluble C substrate supply, or where constraints imposed by the gas-phase diffusion environment restrict O_2 transport (Davidson and Janssens 2006). For example, we have previously observed a similarly large effect of headspace O_2 removal on heterotrophic respiration rates in a peatland Histosol, whereas no immediate effect was observed in a tropical Ultisol collected from the Luquillo Experimental Forest, Puerto Rico (McNicol and Silver 2014). Notably, the predicted y-intercept, which reflects the estimated rate of background anaerobic respiration, was much lower in the log-linear model (126 μg C g^{-1} d^{-1}) than the linear model (186 μg C g^{-1} d^{-1}). This highlights the potential for errors arising from incorrect kinetic characterization of the impact of low O_2 concentrations – such as those found at depth in drained peatlands – on process models that incorporate microbial function. Regardless of fit, absolute rates of predicted anaerobic respiration are higher than

would be expected in C accumulating Histosols. We suggest this is due to high alternative electron acceptor availability, the sapric quality of the peat, and the low water-table position. In particular, the drained deltaic Histosol used in this study has a large acid-extractable Fe pool (>1 mg Fe g^{-1}; McNicol and Silver, unpublished data) that is ~40% Fe(III) at the water-table interface (McNicol and Silver, 2014). The CO_2 emission data suggest that substantial stimulation of CO_2 production may be possible in moist, C-rich Histosols at low O_2 concentrations.

Histosol CH_4 emissions were greatly attenuated at higher O_2 concentrations and this was likely due to a shift toward more aerobic, and fewer anaerobic, soil microsites favoring greater CH_4 consumption, and less CH_4 production overall (Silver et al. 1999; von Fischer and Hedin 2007). Improvements by fitting a log-linear model were particularly apparent for CH_4 emissions and the approximated qkM_{O2} of 0.2 % indicates a very strong O_2 sensitivity. Although we did not experimentally isolate CH_4 consumption, this strong sensitivity to O_2 is consistent with a micro-aerophilic community of methanotrophs (Hanson and Hanson 1996) and observed maxima in gross CH_4 consumption rates immediately above the water table in peatland Histosols where O_2 availability is well below atmospheric concentrations (Sundh et al. 1994; Limpens et al. 2008). Further work is needed to evaluate the short-term O_2 sensitivity of gross CH_4 production and oxidation separately, but these data demonstrate that even very low (< 1%) gas-phase concentrations of O_2 are sufficient to strongly attenuate CH_4 fluxes in wetland soils.

Soil O_2 is increasingly being measured *in situ* (Silver et al. 1999, 2013; Teh et al. 2005; Burgin and Groffman 2012; Hall et al. 2012; Philben et al. 2014). Though O_2 is only one component of the soil redox environment, it is a highly favored oxidant with direct effects on microbial

230 respiration and methanotrophy, and thus may be a useful measurement for linking redox
231 biogeochemistry, microbial ecology, and soil-atmosphere exchange of greenhouse gases
232 (Faulkner et al. 1989; Conrad 1996). In particular the large C pool contained globally in peatland
233 Histosols is maintained by the low availability of O_2 (Freeman et al. 2001; Freeman et al. 2004).
234 Recent modeling efforts show it is necessary to consider the response of aerobic and anaerobic C
235 cycling to the wide range of possible O_2 concentrations in drained soil layers of peatland
236 Histosols (Fan et al. 2014), yet surprisingly few data sets address biogeochemical sensitivity to
237 O_2. We varied O_2 concentration across several orders of magnitude in laboratory incubations of a
238 drained peatland Histosol to investigate the sensitivity of C gas emissions, and in particular the
239 occurrence and importance of non-linearity. We found a log-linear fit best explained the response
240 of CO_2 and CH_4 emissions to O_2 concentration. The results indicate non-linear O_2 effects may be
241 important to consider in soil C biogeochemical models because they predict different background
242 (anaerobic) rates of C emission when compared to linear models, and can capture asymptotic
243 effects of increasing O_2 availability. In summary, the study used a novel O_2 manipulation to
244 identify non-linear relationships between O_2 and Histosol C emissions, and demonstrated the
245 sensitivity of emissions to low O_2 conditions that are often functionally equated with anoxia.
246

247 **Acknowledgements:**
248 This project was supported by the California Delta Stewardship Council via the Delta Science
249 Program. G. M. was supported by a Lawrence Scholarship from Lawrence Livermore National
250 Laboratory. Additional support was provided by UC-AES. We also thank the anonymous
251 reviewers for comments that improved the manuscript.
252

253 **References:**

254 Berner RA (1981) A new geochemical classification of sedimentary environments. Journal of
255 Sedimentary Research 51(2): 359-365

256 Blodau C, Moore TR (2003) Micro-scale CO_2 and CH_4 dynamics in a peat soil during a water
257 fluctuation and sulfate pulse. Soil Biology and Biochemistry 35(4): 535-547

258 Bridgham SD, Megonigal JP, Keller JK, Bliss NB, Trettin C (2006) The carbon balance of North
259 American wetlands. Wetlands 26(4): 889-916

260 Burgin AJ, Groffman PM (2012) Soil O_2 controls denitrification rates and N_2O yield in a riparian
261 wetland. Journal of Geophysical Research: Biogeosciences 117(G1): G01010

262 Chapelle FH, McMahon PB, Dubrovsky NM, Fujii RF, Oaksford ET, Vroblesky DA (1995)
263 Deducing the distribution of terminal electron-accepting processes in hydrologically diverse
264 groundwater systems. Water Resources Research 31(2): 359-371

265 Chimner RA, Cooper DJ (2003) Influence of water table levels on CO_2 emissions in a Colorado
266 subalpine fen: An in situ microcosm study. Soil Biology and Biochemistry 35(3): 345-351

267 Conrad R (1996) Soil microorganisms as controllers of atmospheric trace gases (H_2, CO, CH_4,
268 OCS, N_2O, and NO). Microbiological Reviews 60(4): 609-640

269 Clymo RS (1984) The limits to peat bog growth. Philosophical Transactions of the Royal Society
270 of London. Biological Sciences 303(1117): 605-654

271 Davidson EA, Janssens IA (2006) Temperature sensitivity of soil carbon decomposition and
272 feedbacks to climate change. Nature 440(7081): 165-173

273 Deverel SJ, Rojstaczer S (1996) Subsidence of agricultural lands in the Sacramento-San Joaquin
274 Delta, California: Role of aqueous and gaseous carbon fluxes. Water research 32(8): 2359-2367

Drexler JZ, de Fontaine CS, Deverel SJ (2009) The legacy of wetland drainage on the remaining peat in the Sacramento-San Joaquin Delta, California, USA. Wetlands 29(1): 372-386

Fan Z, Neff JC, Waldrop MP, Ballantyne AP, Turetsky MR (2014) Transport of oxygen in soil pore-water systems: Implications for modeling emissions of carbon dioxide and methane from peatlands. Biogeochemistry 121(3): 455-470

Faulkner SP, Patrick WH, Gambrell RP (1989) Field techniques for measuring wetland soil parameters. Soil Sci. Soc. Am. J. 53(3): 883-890

Freeman C, Ostle N, Kang H (2001) An enzymic 'latch' on a global carbon store. Nature 409(6817): 149-149

Freeman C, Ostle NJ, Fenner N, Kang H (2004) A regulatory role for phenol oxidase during decomposition in peatlands. Soil Biology and Biochemistry 36(10): 1663-1667

Glatzel S, Basiliko N, Moore T (2004) Carbon dioxide and methane production potentials of peats from natural, harvested and restored sites, eastern Québec, Canada. Wetlands 24(2): 261-267

Grable AR, Siemer EG (1968) Effects of bulk density, aggregate size, and soil water suction on oxygen diffusion, redox potentials, and elongation of corn roots. Soil Sci. Soc. Am. J. 32(2): 180-186

Greenwood DJ (1961) The effect of oxygen concentration on the decomposition of organic materials in soil. Plant and Soil 14(4): 360-376

Hall SJ, McDowell WH, Silver WL (2012) When wet gets wetter: Decoupling of moisture, redox biogeochemistry, and greenhouse gas fluxes in a humid tropical forest soil. Ecosystems 16(4): 576-589

Hanson RS, Hanson TE (1996) Methanotrophic bacteria. Microbio Mol Biol R 60(2): 439-463

298 Hatala JA, Detto M, Sonnentag O, Deverel SJ, Verfaillie J, Baldocchi DD (2012) Greenhouse
299 gas (CO_2, CH_4, H_2O) fluxes from drained and flooded agricultural peatlands in the Sacramento-
300 San Joaquin Delta. Agriculture, Ecosystems and Environment 150: 1-18
301 Jungkunst HF, Fiedler S (2007) Latitudinal differentiated water table control of carbon dioxide,
302 methane and nitrous oxide fluxes from hydromorphic soils: feedbacks to climate change. Global
303 change biology 13(12): 2668-2683
304 Kasimir-Klemedtsson Å, Klemedtsson L, Berglund K, Martikainen P, Silvola J, Oenema O
305 (1997) Greenhouse gas emissions from farmed organic soils: a review. Soil Use and
306 Management 13: 245-250
307 Laiho R (2006) Decomposition in peatlands: Reconciling seemingly contrasting results on the
308 impacts of lowered water levels. Soil Biology and Biochemistry 38(8): 2011-2024
309 Limpens J, Berendse F, Blodau C, Canadell JG, Freeman C, Holden J, Roulet N, Rydin H,
310 Schaepman-Strub G (2008) Peatlands and the carbon cycle: from local processes to global
311 implications – a synthesis. Biogeosciences 5(5): 1475-1491
312 Liptzin D, Silver WL, Detto M (2010) Temporal dynamics in soil oxygen and greenhouse gases
313 in two humid tropical forests. Ecosystems 14(2): 171-182
314 McNicol G, Silver WL (2014) Separate effects of flooding and anaerobiosis on soil greenhouse
315 gas emissions and redox sensitive biogeochemistry. Journal of Geophysical Research:
316 Biogeosciences 119(4): 2013JG002433
317 Moore TR, Dalva M (1993) The influence of temperature and water table position on carbon
318 dioxide and methane emissions from laboratory columns of peatland soils. Journal of Soil
319 Science 44(4): 651-664

320 Moore S, Evans CD, Page SE, Garnett MH, Jones TG, Freeman C, Hooijer A, Wiltshire AJ,
321 Limin SH, Gauci V (2013) Deep instability of deforested tropical peatlands revealed by fluvial
322 organic carbon fluxes. Nature 493(7434): 660-663
323 Moore TR, Knowles R (1989) The influence of water table levels on methane and carbon dioxide
324 emissions from peatland soils. Canadian Journal of Soil Science 69(1): 33-38
325 Myhre G, Shindell D, Bréon F-M, Collins W, Fuglestvedt J, Huang J, Koch D, Lamarque J-F,
326 Lee D, Mendoza B, Nakajima T, Robock A, Stephens G, Takemura T, and Zhang H, (2013)
327 Anthropogenic and Natural Radiative Forcing. In: Climate Change 2013: The Physical Science
328 Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental
329 Panel on Climate Change [Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J,
330 Nauels A, Xia Y, Bex V, and Midgley PM, (eds.)]. Cambridge University Press, Cambridge,
331 United Kingdom and New York, NY, USA.
332 Nieveen JP, Campbell DI, Schipper LA, Blair IJ (2005) Carbon exchange of grazed pasture on a
333 drained peat soil. Global change biology 11(4): 607-618
334 Oleszczuk R, Truba M (2013) The analysis of some physical properties of drained peat-moorish
335 soil layers. Annals of Warsaw University of Life Sciences – SGGW. Land Reclamation 45(1):
336 41-48
337 Philben M, Kaiser K, Benner R (2014) Does oxygen exposure time control the extent of organic
338 matter decomposition in peatlands? Journal of Geophysical Research: Biogeosciences 119(5):
339 2013JG002573
340 Ruel JJ, Ayres MP (1999) Jensen's inequality predicts effects of environmental variation. Trends
341 in Ecology and Evolution 14(9): 361-366

342 Schothorst CJ (1977) Subsidence of low moor peat soils in the western Netherlands. Geoderma
343 17(4): 265-291
344 Scott Michael J, Morgan James J (1990) Energetics and conservative properties of redox
345 systems. In: Chemical Modeling of Aqueous Systems II. ACS Symposium Series, vol 416.
346 American Chemical Society. pp 368-378
347 Silver WL, Lugo AE, Keller M (1999) Soil oxygen availability and biogeochemistry along
348 rainfall and topographic gradients in upland wet tropical forest soils. Biogeochemistry 44(3):
349 301-328
350 Silver W, Liptzin D, Almaraz M (2013) Soil redox dynamics and biogeochemistry along a
351 tropical elevational gradient. Ecol. Bull 4: 195-209
352 Silvola J, Alm J, Ahlholm U, Nykanen H, Martikainen PJ (1996) CO_2 fluxes from peat in boreal
353 mires under varying temperature and moisture conditions. Journal of Ecology 84(2): 219-228
354 Sundh I, Nilsson M, Granberg G, Svensson BH (1994) Depth distribution of microbial
355 production and oxidation of methane in northern boreal peatlands. Microbial ecology 27(3): 253-
356 265
357 Sulman BN, Desai AR, Cook BD, Saliendra N, Mackay DS (2009) Contrasting carbon dioxide
358 fluxes between a drying shrub wetland in Northern Wisconsin, USA, and nearby forests.
359 Biogeosciences 6(6): 1115-1126
360 Teh YA, Silver WL, Conrad ME (2005) Oxygen effects on methane production and oxidation in
361 humid tropical forest soils. Global Change Biology 11(8): 1283-1297
362 Teh YA, Silver WL, Sonnentag O, Detto M, Kelly M, Baldocchi DD (2011) Large greenhouse
363 gas emissions from a temperate peatland pasture. Ecosystems 14(2): 311-325

von Fischer JC, Hedin LO (2007) Controls on soil methane fluxes: Tests of biophysical mechanisms using stable isotope tracers. Global Biogeochemical Cycles 21(2): GB2007

Whalen SC (2005) Biogeochemistry of methane exchange between natural wetlands and the atmosphere. Environmental Engineering Science 22(1): 73-94

Tables:

Soil Classification	**Site Location**	**C/N** (%)	**Moisture** (%)	**Bulk Density** (g cm^{-3})	**Porosity***
Typic Haplosaprists	Sherman Island, CA	23.7 ± 3.0/ 1.1 ± 0.1	62 ± 1	0.25	0.84

Table 1 Soil classification and characteristics at 80 cm depth in profile (mean ± SE).

*Porosity estimated using assumed sapric peat particle density of 1.6 g cm^{-3} (Oleszczuk and Truba, 2013)

Gas	Fit	p-value	R^2	Y-intercept ($\mu g\ C\ g^{-1}\ d^{-1}$)	O_2 Effect (%)	*q*Vmax ($\mu g\ C\ g^{-1}\ d^{-1}$)	*q*kM_{O2} (%)
CO_2	Linear	< 0.001	0.38	186	+24	-	-
	Log	< 0.001	0.49	126	+75	-	-
	MM	-	-	-	-	47.3	2.2
CH_4	Linear	< 0.001	0.40	0.21	-257	-	-
	Log	< 0.001	0.70	0.42	-383	-	-
	MM	-	-	-	-	-0.18	0.2

Table 2 Coefficients and fits of linear, log-linear (Log), and Michaelis-Menten (MM) models

Captions

Fig. 1. Average O_2 concentrations (mean ± 1 SD) with depth (10, 20, 30 cm) in drained peatland pasture Sherman Island, CA, collected hourly (n = 744) in March 2012

Fig. 2. CO_2 flux (a, b; $\mu g\ C\ g^{-1}\ d^{-1}$) and CH_4 flux (c, d; $ng\ C\ g^{-1}\ d^{-1}$) versus O_2 concentration ($[O_2]$ (ppm(v))) on untransformed x-axis (a, c) and $\log_{10}$ transformed (b, d) x-axis. Dashed line, coefficients, R^2 and p-values are for log-linear model fit