

## Soil redox dynamics and biogeochemistry along a tropical elevation gradient

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Soil oxygen ( $O_2$ ) availability and associated redox-sensitive biogeochemistry have the potential to structure biotic communities along humid tropical elevation gradients. However, few long-term data exist on soil  $O_2$  concentrations in tropical forests, or linkages between redox and carbon (C) and nutrient cycling. We report on an eight year study of soil  $O_2$  concentrations along a montane elevation gradient in the Luquillo Experimental Forest, Puerto Rico. We also present a conceptual model that links redox dynamics with key biogeochemical processes and review research on redox-sensitive biogeochemistry along the same gradient.

Soil  $O_2$  concentrations varied significantly over time and space along the gradient. Most sites experienced periodic anoxia. Upper elevation palm forests experienced the lowest average soil  $O_2$  availability ( $10.5 \pm 0.2\%$ ) and the highest frequency of low redox events, with one third of the measurements at or below 3%  $O_2$ . There was significant temporal coherence among forest types and strong correlations among sites. There was also significant periodicity in soil  $O_2$  at short (two week) and long (monthly to seasonally) time scales. The detectable seasonality in the long-term record was surprising given that these forests are generally considered aseasonal. Soil  $O_2$  was positively correlated with bulk density, and negatively related to soil C and N concentrations along the gradient. The timing of rainfall was a good predictor of soil  $O_2$  concentrations at short temporal scales, while the magnitude of rainfall was strongly correlated with  $O_2$  at longer time scales.

The spatial and temporal patterns in soil redox dynamics along the elevation gradient were used to construct hypothetical predictions of key nitrogen (N), iron (Fe), and carbon (C) transformations. A review of the literature suggested that the relatively low potential nitrous oxide ( $N_2O$ ) fluxes from these soils contrasts with the higher potential for dissimilatory nitrate reduction to ammonium ( $NH_4^+$ ), which is a lower redox pathway that rapidly consumes nitrate ( $NO_3^-$ ) and thus depletes the substrate for denitrification. Iron cycling appeared to be particularly important along the gradient due to the Fe-rich soils, large number of iron-reducing microbes and rapid fluctuations between oxidized and reduced states. Iron redox-cycling was increasingly important for C respiration and phosphorus (P) availability with elevation. Low redox events drove considerable methane emissions at the top of the elevation gradient. Our results highlight the sensitivity of montane forests to climate and indicate that changes in the timing and amount of rainfall are likely to feed back on soil  $O_2$  availability, nutrient cycling, C storage, and trace gas emissions.

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Tropical montane elevation gradients are often characterized by dramatic changes in plant community composition, vegetation structure, and net primary productivity (Grubb 1977, Tanner et al. 1992, Silver et al. 1999, Giardin et al. 2010, Hillyer and Silman 2010). There are likely several factors that contribute to these patterns with elevation including decreasing temperature and increasing cloudiness, leading to lower light availability (Grubb 1977, Moser et al. 2007). Soil nutrient availability, Fe toxicity, and soil

oxygen ( $O_2$ ) limitation have also been cited as possible factors contributing to changes along tropical elevation gradients (Grubb 1977, Tanner et al. 1992), although few studies have measured these variables. This is particularly true for soil  $O_2$  and associated redox dynamics which are closely linked with many biogeochemical processes.

Humid tropical forests experience continuous warm temperatures and abundant moisture throughout the year. These conditions, coupled with finely textured clay soils

and high biological O<sub>2</sub> demand facilitate the periodic depletion of O<sub>2</sub> in surface soils where O<sub>2</sub> consumption by plants and microorganisms exceeds the rate of diffusive resupply (Silver et al. 1999). Fluctuating O<sub>2</sub> concentrations are associated with changes in redox potential (Faulkner and Patrick 1992, Schuur et al. 2001). Redox dynamics can affect many biological and biogeochemical processes in terrestrial ecosystems. For example, decreased soil O<sub>2</sub> concentrations have long been known to cause physiological stress to most plants (Vartapetian and Jackson 1997) and can alter the amount and availability of key nutrient resources in soils (Faulkner and Patrick 1992, Silver et al. 1999, 2001, Chacon et al. 2006, Liptzin and Silver 2009). Fluctuating redox potential can also affect the production and consumption of trace gases such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O). These greenhouse gases play an important role in radiative forcing in the atmosphere.

Few studies have measured O<sub>2</sub> concentrations and dynamics in humid tropical soils and linked these with biogeochemical cycling (Silver et al. 1999, Liptzin et al. 2011). These studies have shown that soil O<sub>2</sub> can vary dramatically over short time periods and across soil microsites. Climate is assumed to be the primary driver of fluctuating O<sub>2</sub> in upland soils. Temperature inversely affects O<sub>2</sub> solubility in water. While temperature can be an important driver of O<sub>2</sub> availability in temperate and boreal systems, tropical soils are typically characterized by near constant warm temperatures. In contrast, patterns in precipitation and soil moisture are likely to have strong impacts on O<sub>2</sub> availability in humid tropical ecosystems. Moisture affects soil O<sub>2</sub> by coating surfaces and filling pore spaces, which decreases rates of diffusive gas transport in soils. Soil texture, structure, and organic matter content play important roles in soil redox dynamics by affecting the amount and residence time of water in soils. Similarly, the evaporative potential at the soil surface indirectly feeds back on soil O<sub>2</sub> through impacts on soil moisture and water-filled pore space. Biological activity also plays an important role in soil O<sub>2</sub> concentrations. High biological activity typical of humid tropical forests can deplete soil O<sub>2</sub> through respiratory processes (primarily roots and microbes) even in well-drained soils (Silver et al. 1999). Invertebrates and root channels can increase soil O<sub>2</sub> availability through the formation of macropores.

The upper montane elevation gradient of the Luquillo Experimental Forest (LEF), Puerto Rico is an excellent system to explore patterns in soil O<sub>2</sub> availability and redox-sensitive biogeochemical cycling. Similar to other tropical mountains, plant species composition changes, canopy heights decrease, and net primary production declines with increasing elevation (Weaver and Murphy 1990, Weaver 1994). Unlike mainland mountains, the ecological changes along the upper LEF gradient are compressed into a relatively narrow (400 m) elevation range typical of tropical islands (Grubb 1971). This effectively decreases

the importance of temperature change as a major driving variable along the gradient.

In this paper we explore patterns in soil O<sub>2</sub> availability and redox-sensitive biogeochemistry along the upper LEF elevation gradient. We present data from a long-term (eight year) record of soil O<sub>2</sub> concentrations from 12 plots in four montane tropical forest types, by far the longest continuous record of soil O<sub>2</sub> measurements. We explore patterns in soil O<sub>2</sub> availability in space and time and compare these with patterns in soil chemical and physical properties and precipitation. The study of soil O<sub>2</sub> along the LEF gradient has provided the context for exploring redox-sensitive biogeochemistry in soils and across the soil-atmosphere interface. We present a simple conceptual model linking redox dynamics with key biogeochemical processes, and review the literature on redox-related cycling of C, nitrogen (N), iron (Fe), and phosphorus (P) along this elevation gradient.

## Study site and approach

### The elevation gradient

The research sites were part of the NSF sponsored Long Term Ecological Research project in Puerto Rico. Soil O<sub>2</sub> was sampled in 12 plots that spanned from 635 to 968 m a.s.l. within an area of ca 435 ha (Lugo pers. comm.). Several biogeochemical pools and processes were measured at points along this upper elevation gradient as well as a longer gradient that included the tabonuco forest type at 350 m a.s.l. (Silver et al. 1999).

Plots were ca 30 × 10 m in size and were situated on slopes on the windward side of the LEF. Plots were separated by landforms (i.e. small ridges, valleys) that eliminated the possibility of drainage across plots and were several hundreds of meters to several kilometers apart. Replicate plots (n = 3) were located in each of four forest types: colorado forest (COL) at 635, 731, 741 m a.s.l., palm dominated forest (PAL) at 806, 858, 903 m a.s.l., tall cloud forest (TCF) at 871, 915, 930 m a.s.l., and short cloud forest (SCF) 949, 967, 968 m a.s.l. Colorado and palm forest follow the nomenclature of Weaver (1991, 1994). We subdivided the cloud forest into two categories based on tree species composition and canopy height. The short cloud forest had average canopy heights of 3 ± 0.3 m, and was dominated by *Tabebuia rigida* with an importance value of 43–68%. Canopy heights of tall cloud forest were 5 ± 0.3 m, and *Ocotea spatulata* and *Micropholis garciniifolia* dominated with importance values of 45–55%. Palm forest was dominated by *Prestoea montana* (51–80% importance values). In the colorado forest, the dominant species was *Clusia clusioides* (importance value of 32% at 731 and 741 m a.s.l.) and a combination of five species in the lower elevation plot, each contributing between 14 and 19% of

the importance value: *Calycogonium squamulosum*, *Cordia borinquensis*, *Magnolia splendens*, *Micropholis garciniifolia*, *Prestoea montana*.

Soils in the LEF are derived from volcanoclastic sediments with quartz diorite intrusions (Beinroth 1982). The study sites were located on volcanoclastic sediments with a high clay content (up to 70%), with the possible exception of sites in the colorado forest which occurred near the contact between the volcanoclastic and dioritic sediments. The forest sites used here were growing on a thick clay cap (> 1 m) above a clay loam (Silver et al. 1999, McGroddy and Silver 2000). Soils are predominantly classified as ultisols (lower elevation) and oxisols (upper elevation) (Scatena 1989, USDA NRCS 2002). Mean daily temperature decreased from approximately 21°C at 635 m a.s.l. to 19.5°C at 968 m a.s.l. (Silver et al. unpubl.).

Precipitation was measured over the study period using four tipping bucket rain gauges (Texas Electronics TE-525) located near the research plots at 741 m a.s.l. (colorado forest), 858 m a.s.l. (palm forest), 930 m a.s.l. (tall cloud forest), and 968 m a.s.l. (short cloud forest). Rainfall in upper montane forests is often underestimated due to irregular episodes of horizontal precipitation (Still et al. 1999), which may be occurring here. For that reason the absolute magnitude of rainfall should be interpreted with caution as values are an approximation. As all four montane climate stations had a clear windward exposure on the ridgeline, they likely experienced similar horizontal precipitation events. Thus, the timing and relative magnitude of precipitation across sites is well constrained. We compared total annual rainfall with mean annual soil O<sub>2</sub> for each forest type. For annual rainfall totals, missing data were estimated using linear regressions with other nearby stations. Non-parametric correlations were calculated using ranked daily precipitation totals for each pair of stations. The Spearman R values ranged from 0.76 to 0.95 with all stations having another correlated station with a Spearman R of at least 0.85. In two cases, a 14 d period in 1995 and a 10 d period in 1997, all of the stations were offline due to hurricane warnings. During these time periods we used the mean annual daily rainfall for each station to replace missing data.

## Soil oxygen

Soil O<sub>2</sub> was measured every two weeks from August 1994 to October 2002 (n = 204 time points per chamber). Soil equilibration chambers (n = 5 per plot, total n = 60) consisted of 60 ml inverted polypropylene centrifuge tubes fitted with 1/8 in copper tubing and sealed with a three-way stopcock (Silver et al. 1999). All junctures were sealed against leakage with a heavy application of automotive goop. To insert the chambers into the soil, a small bore hole was excavated to ca 10 cm depth. The chamber was then inserted into the hole and pushed down another 2–4

cm to assure good contact with the soil. The remaining space in the hole was then backfilled with soil so that all that was protruding from the surface was the copper tubing and stopcock. The chambers were then left for several weeks to equilibrate in the 0–10 cm depth; re-equilibration after sampling was generally rapid on the scale of 1 to 3 d (Liptzin et al. 2011). Sample gases were collected by first drawing and expelling 5–10 ml of gas with a syringe to clear the tubing dead space, and then taking a 40 ml gas sample from each chamber, which was analyzed immediately in the field on a YSI O<sub>2</sub> meter (model 51B) and Clark-type electrode. The O<sub>2</sub> electrode was adapted with an air-tight cell with two ports, allowing for sample analysis without exposure to ambient air (Patrick 1977, Faulkner et al. 1989). We chose to use a 40 ml sample volume after determining that the dead space volume in the air tight cell was < 3 ml, and that the meter required a minimum of 30 ml to achieve a stable O<sub>2</sub> reading. After determining the sample concentration, the electrode cell was flushed with ambient air until the O<sub>2</sub> meter response reached atmospheric concentrations (21%).

## Soil characteristics

Soil C and N concentrations were measured in the 0–10 cm depth in each plot along the elevation gradient. Soil cores were sampled from five random locations within each plot using a 2.5 cm diameter corer (n = 60). Multiple cores (4–6) were collected within a 1 m area at each sampling location and placed in the same bag. Samples were run in duplicate for C and N on an elemental analyzer at U.C. Berkeley.

Bulk density was sampled in the 0–10 cm depth at three randomly located sites within each plot (n = 36). We carefully extracted soils using a 4.1 cm diameter corer. Samples were brought to the lab, dried at 105°C until they reached a constant weight, and then weighed. Bulk density was calculated as the mass of dry soil per volume and are reported in g cm<sup>-3</sup>. We encountered no large roots or rocks in these surface samples.

## Statistical analyses and modeling

We calculated the average soil O<sub>2</sub> concentrations of the five replicate chambers in each plot over time to identify patterns along the elevation gradient and among forest types. We compared average annual soil O<sub>2</sub> concentrations of the forest types, with plot averages as replicates, using analysis of variance (ANOVA). If data did not conform to the assumptions of ANOVA they were log transformed. Values are reported as means ± 1 standard error unless otherwise noted. We calculated the cumulative probability of soil O<sub>2</sub> concentrations per plot and by forest type using 1% increments of O<sub>2</sub> from 0 to 21%. We used cross correlation

analyses to test if there were lags among forest types in soil O<sub>2</sub> dynamics. All statistical analyses were performed using Systat 11 (Systat Software, Chicago, IL).

We calculated the average soil O<sub>2</sub> for each forest type (COL, PAL, TCF, SCF) for each two week period. Missing values were filled with linear interpolation. We summed daily precipitation to calculate total precipitation for the same two week periods. We used these data to explore monthly and seasonal relationships between O<sub>2</sub> and precipitation. We calculated a three month (13 weeks) centered moving average to evaluate the interannual patterns in the O<sub>2</sub> and precipitation time series. Smoothing the data deemphasizes the time lag exhibited at shorter time scales and allowed us to explore monthly and intra-annual patterns.

We used wavelet analysis to evaluate the spectral properties of the unsmoothed time series and the relationship of soil O<sub>2</sub> and precipitation. Wavelet analysis, similar to Fourier analysis, breaks up the variance in the time series to estimate the relative contributions at a range of temporal scales (Cazelles et al. 2008). We used Matlab code avail-

able online <<http://paos.colorado.edu/research/wavelets/software.html>> to calculate the continuous wavelet spectra in the time-frequency domain. We used the Morlet wavelet as the mother wavelet and padded with zeroes to reduce errors at the beginning and end of the time series (Torrence and Compo 1998). The cone of influence indicates the region where the results may be unreliable because of edge effects. We calculated the global wavelet power spectra, the analog of Fourier spectra, as the time average of the wavelet spectra. To examine relationships in soil O<sub>2</sub> and precipitation, we calculated wavelet coherence (WC). The WC can be thought of as the spectral correlation between two time series and, equivalent to the R<sup>2</sup>, can vary between 0 and 1. Importantly, WC finds regions in the frequency space where two time series co-vary, regardless of whether they have high common power (Grinsted et al. 2004, Yates et al. 2007, Cazelles et al. 2008). The WC was calculated, along with a 95% confidence level using Monte Carlo Simulation with 1000 surrogates, based on Matlab code available online <[www.pol.ac.uk/home/research/wavelet-coherence/](http://www.pol.ac.uk/home/research/wavelet-coherence/)>.

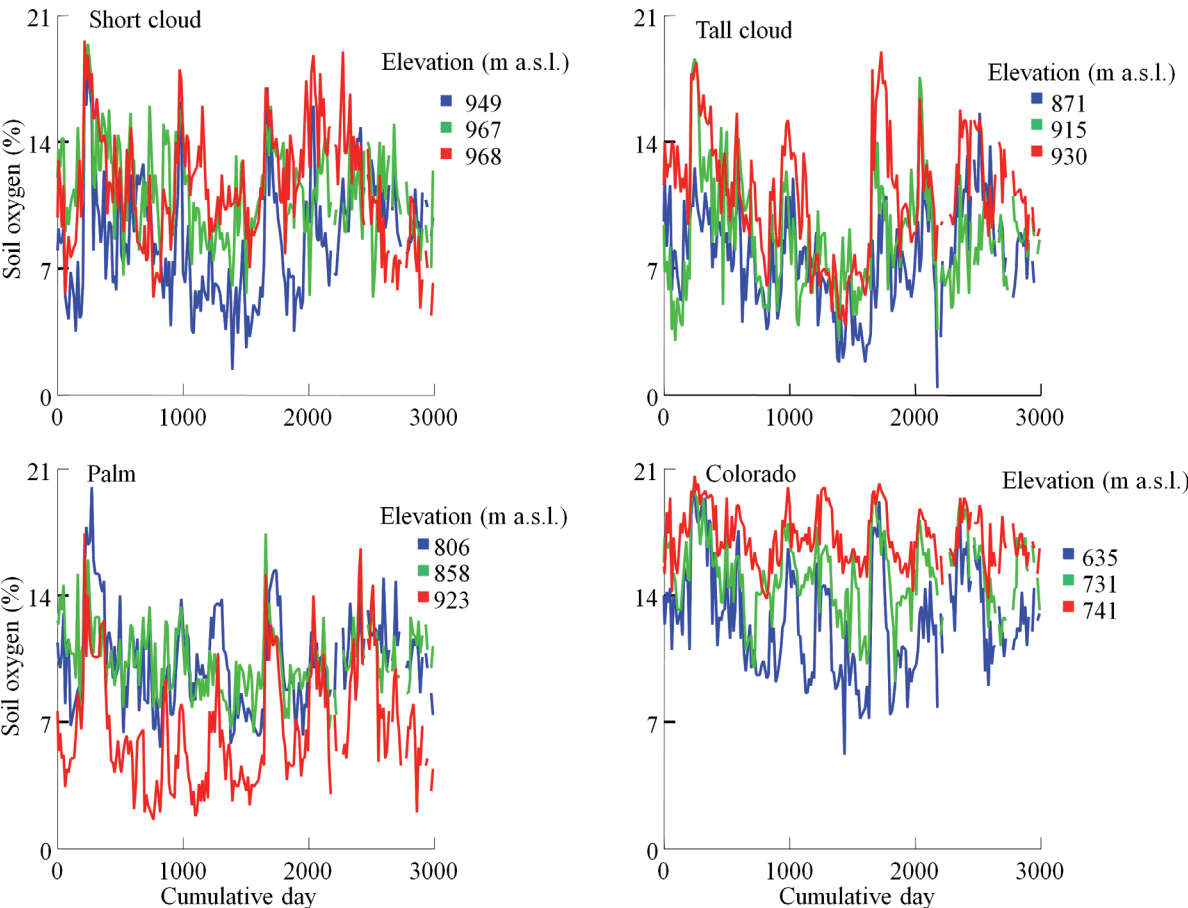


Figure 1. Soil O<sub>2</sub> concentrations (1994–2002) along an elevation gradient in the Luquillo Experimental Forest, Puerto Rico. Values are means of 5 chambers per plot per sampling period.

## Results and discussion

### Spatial patterns in soil oxygen availability

Soil  $O_2$  concentrations were highly variable in space and time along the elevation gradient (Fig. 1). Individual chambers fluctuated from near atmospheric concentrations (21%) to  $< 5\%$  during 2–4 week periods. Most chambers experienced periods of low  $O_2$  availability over the study and 33 of 60 chambers had periods of severe anoxia characterized by  $\leq 1\%$   $O_2$ . Only one of 12 plots, the colorado forest plot at 731 m, never experienced an average soil  $O_2$  concentration of  $< 1\%$ . All sites experienced some oxic periods (soil  $O_2 \geq 20\%$ ). The upper elevation palm forest had the lowest average soil  $O_2$  concentrations ( $10.5 \pm 0.2\%$ ). The three colorado forest plots had significantly higher average soil  $O_2$  concentrations ( $12.7 \pm 0.2$  to  $17.2 \pm 0.1\%$ ) than the other forest types for the eight years of study ( $p < 0.001$ , Fig. 2).

The cumulative probability of soil  $O_2$  concentrations differed along the elevation gradient (Fig. 3a). The high elevation palm forest (923 m a.s.l.) had the greatest probability of low  $O_2$  concentrations with ca 55% of the observations  $\leq 5\%$   $O_2$ , a level that is likely to stress aerobic respiration of upland plants (Crawford 1989). Approximately 33% of the observations in the high elevation palm plot were  $\leq 3\%$   $O_2$ , which has been identified as a critical  $O_2$  threshold for wetland plants (Drew 1990). The colorado forest plot at 741 m a.s.l. had the lowest cumulative probability of anoxic conditions with  $> 70\%$  of the measurements  $\geq 15\%$  soil  $O_2$ . When examined by forest type, the short and tall cloud forests and palm forest had similar cumulative probabilities of soil  $O_2$  concentrations, and all three differed from the colorado forest (Fig. 3b).

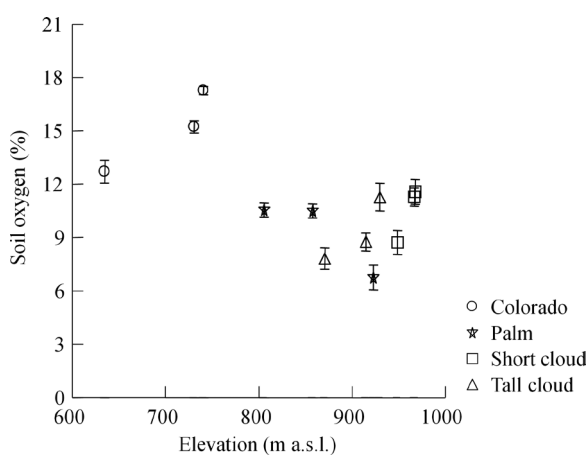


Figure 2. Soil  $O_2$  concentrations over the 8-yr study by elevation in the Luquillo Experimental Forest, Puerto Rico. Values are means and standard errors.

Soil  $O_2$  availability and associated redox dynamics are controlled by a suite of variables that act at microsite to landscape scales. For example, plant and microbial activity (McKee 1993, Pett-Ridge and Firestone 2005), topography (Silver et al. 1999, Teh et al. 2011), and bulk density (Keller and Reiners 1994) are all factors that can affect soil redox. Average soil  $O_2$  concentrations were significantly positively correlated with bulk density along the elevation gradient ( $r^2 = 0.65$ ,  $p < 0.01$ ,  $n = 12$ , Fig. 4a). Bulk density ranged from  $0.28 \pm 0.02$  in the upper elevation palm forest (923 m a.s.l.) to  $0.74 \pm 0.11$  in the colorado forest (741 m a.s.l.); the colorado forest had significantly higher bulk density than the other forest types ( $p < 0.01$ , Fig. 4b). Very low bulk density is often associated with organic rich soils with high water holding capacity and low redox potential (Bridgman et al. 1998). The very low bulk densities in some of the higher elevation sites were likely due to high organic matter content in these soils. Soil C concentrations increased significantly along the elevation gradient ( $r^2 = 0.65$ ,  $p < 0.01$ ). Soil organic matter and associated C concentrations can be very sensitive to small changes in temperature (Townsend et al. 1992) and redox potential (Day and Megonigal 1993). Although the variation in mean daily temperature is small among this gradient (ca  $2^\circ\text{C}$ ) it may be sufficient to inhibit decomposition when coupled with high precipitation and frequent low redox conditions, leading to C-rich soils. Soil  $O_2$  was weakly negatively correlated with soil C concentrations ( $r^2 = 0.34$ ,  $p < 0.01$ , Fig. 4c) and there was no significant relationship with C content. Soil C and N concentrations were significantly positively correlated ( $r^2 = 0.91$ ,  $p < 0.01$ ). Similar to C, total soil N was negatively correlated with soil  $O_2$  ( $r^2 = 0.49$ ,  $p = 0.01$ , Fig. 4d).

### Temporal patterns of soil oxygen

To identify temporal coherence in soil  $O_2$  concentrations across the landscape we used cross correlation analyses. Soil  $O_2$  concentrations were positively correlated among all forest types for instantaneous measurements (i.e. with zero time lag). The instantaneous measurements were always the most strongly correlated (Pearson correlation coefficients of 0.7–0.9), but the correlations remained significant at longer time scales. Soil  $O_2$  concentrations in the short and tall cloud forests were significantly positively correlated for a lag of up to eight weeks, while the correlation between tall cloud forest and palm forest  $O_2$  was significant for a lag of 16 weeks. The strong instantaneous correlation among sites suggests considerable coherence and likely reflects responses to regional weather events. The decreasing strength of correlations over time likely results from local scale phenomena affecting diffusion into and out of soils, as well as  $O_2$  consumption rates.

After smoothing the data over three month intervals, all four forest types showed clear seasonal and interannual

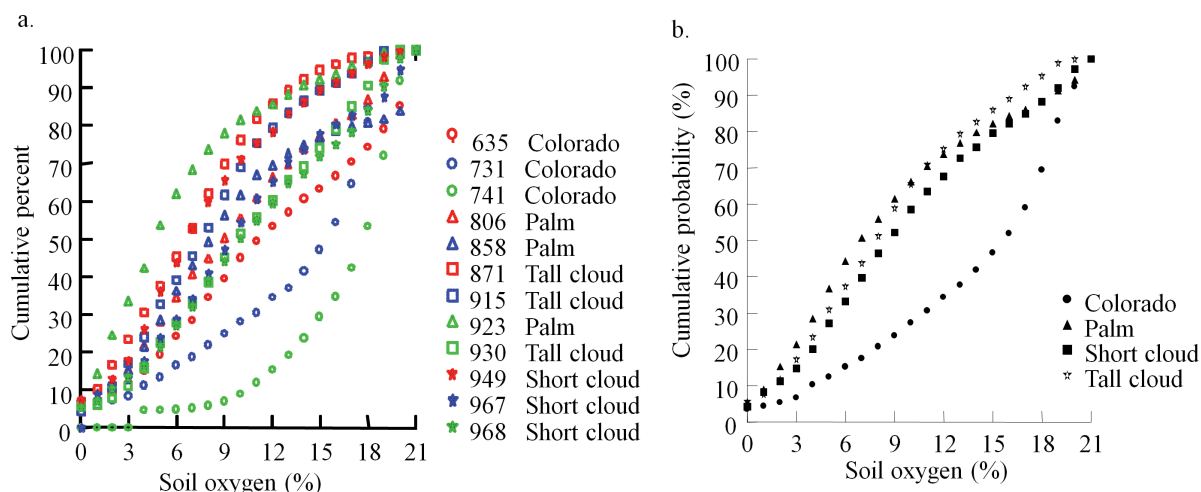


Figure 3. Cumulative probabilities of soil O<sub>2</sub> concentrations by elevation (a) and forest type (b) in the Luquillo Experimental Forest, Puerto Rico.

patterns (Fig. 5). The wavelet analysis corroborated the strong seasonal cycle in soil O<sub>2</sub>: there was a strong peak at one year in the global power spectra in all four sites (Fig. 6). Based on the smoothed data, soil O<sub>2</sub> tended to be highest in spring and lowest in the fall. For example, the monthly means of the smoothed data for all the TCF chambers ranged from a high of 13.2% in May and a low of 9.5% in November (Fig. 7). Liptzin et al. (2011) measured hourly soil O<sub>2</sub> over several months in surface soils in a nearby tall cloud forest site at 930 m a.s.l. in the LEF. While this record is much shorter, it also exhibited the seasonal trend of higher O<sub>2</sub> in the spring and lower O<sub>2</sub> in the fall (Fig. 7). In addition, the shorter term (~two week) fluctuations were evident from the high frequency samples that are not detectable in the longer term record that was sampled twice monthly.

### Relationship of soil oxygen and precipitation

Mean monthly soil O<sub>2</sub> was strongly negatively correlated ( $r^2 = 0.80$ ,  $p < 0.01$ ) to mean monthly precipitation when both data sets were averaged across years (Fig. 8a). The seasonal pattern of precipitation was the opposite of soil O<sub>2</sub>. Averaged across the gradient, precipitation was lowest in spring and greatest in fall (Fig. 8b). The temporal relationship between soil O<sub>2</sub> and precipitation was examined with wavelet coherence and similar among the four forest types. Using the TCF as an example, the wavelet coherence was significant at periods of one year for most of the time series (Fig. 9). The two time series were typically 180° out of phase, illustrating the negative correlation between rainfall and soil O<sub>2</sub> concentrations.

Liptzin et al. (2011) used continuous sensor measurements in a tall cloud forest site at 930 m in the LEF to

explore short-term dynamics in soil O<sub>2</sub> in relation to rainfall. They found that soil O<sub>2</sub> fluctuated at two week intervals. The fluctuations in soil O<sub>2</sub> were best predicted by the timing, and not the magnitude of precipitation. During short-term dry periods ( $< 1 \text{ mm d}^{-1}$  for 5–8 d), soil O<sub>2</sub> increased rapidly. Soil O<sub>2</sub> began to decrease almost to the hour when rainfall started again and would continue to decrease as long as the precipitation continued. Thus, over time scales of hours to days, the timing of precipitation drives fluctuations in O<sub>2</sub>, but at longer time scales, the amount of precipitation determines the long-term average O<sub>2</sub> concentration. Finally, the effect of precipitation can be modulated by the soil conditions, specifically bulk density and organic matter content.

## Redox-sensitive biogeochemical cycling

### The role of fluctuating redox in soils

Redox reactions drive many important biogeochemical processes in soils. As soil O<sub>2</sub> concentrations decrease NO<sub>3</sub><sup>-</sup>, Fe, manganese (Mn), sulfate (SO<sub>4</sub><sup>2-</sup>), and C become increasingly important as alternative electron acceptors with consequences for soil nutrient availability and greenhouse gas emissions. We have shown that soil O<sub>2</sub> concentrations can fluctuate rapidly in tropical forests, on daily to bi-weekly timescales. The effects of fluctuating redox on biogeochemical cycling are likely to differ from those in more static redox environments. Fluctuating redox can result in rapid pulsing of oxidized and reduced states that can increase the bio-availability of nutrients such as P (DeAngelis et al. 2010) or increase nutrient losses (e.g. denitrification, Pett-Ridge et al. 2006, leaching, McGroddy et al. 2008).

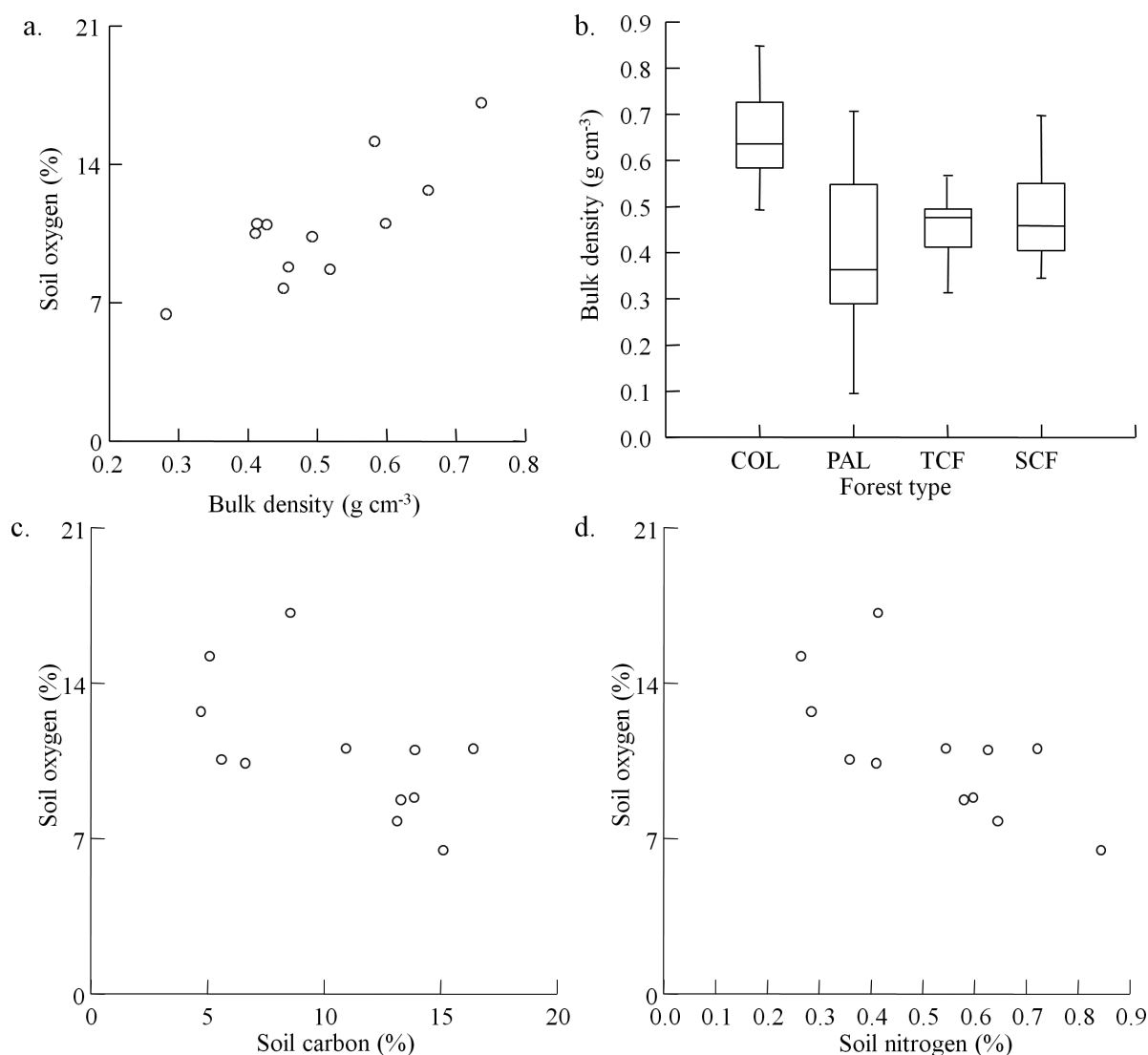


Figure 4. (a) Relationship between soil O<sub>2</sub> concentrations and bulk density (0–10 cm depth) along the upper elevation gradient in the LEF. (b) Variability in soil bulk density among the four forest types in the upper elevations of the LEF. The center horizontal line is the median, the length of the box is the range of data within which the central 50% of the values fall, with hinges at the first and third quartiles. (c) Relationship between soil O<sub>2</sub> concentrations and soil C concentrations (0–10 cm depth) along the upper elevation gradient in the LEF. (d) Relationship between soil O<sub>2</sub> concentrations and soil N concentrations (0–10 cm depth) along the upper elevation gradient in the LEF.

We present a simple conceptual model of potential patterns in key redox-sensitive biogeochemical processes in a humid tropical forest using the short-term O<sub>2</sub> record (Fig. 10a) from Liptzin et al. (2011) and the longer-term record reported here (Fig. 10b). Over the short-term, rapid fluctuation in redox on the scale of days to weeks are characterized by pulses of reducing events of different magnitudes. Over the longer-term, it becomes clear that some months are more likely than others to experience reducing events, and that there is considerable interannual variability. At both time scales, the biogeochemical

dynamics at intermediate redox potentials are likely to dominate, which in this system are likely driven by Fe reduction and reoxidation. It is important to note that average soil O<sub>2</sub> concentrations occur as a result of a distribution of microsite conditions, where most biogeochemical transformations occur. Lower bulk soil O<sub>2</sub> concentrations generally represent a higher proportion of anaerobic microsites and thus lower redox conditions in general (Silver et al. 1999).

The dynamics of N, Fe, and C provide a generalized view of potential biogeochemical sensitivities to fluctuat-

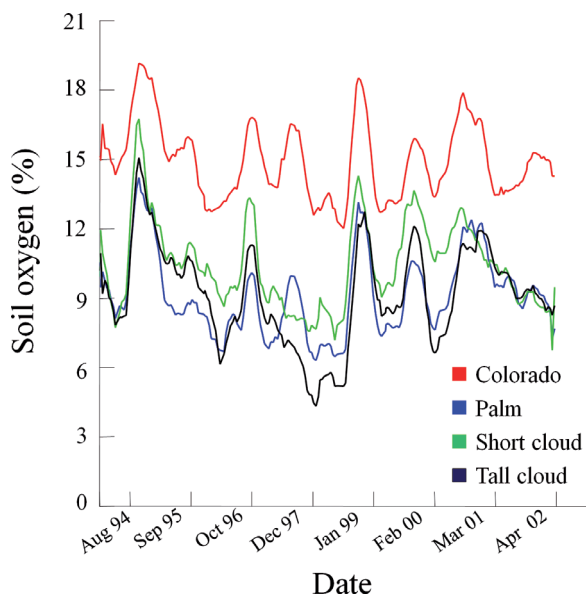


Figure 5. Smoothed soil  $O_2$  concentrations along the elevation gradient by forest type in the Luquillo Experimental Forest, Puerto Rico. Data were smoothed by chamber within each plot using 12-week running averages, and then averaged by forest type.

ing  $O_2$  concentrations. Nitrate reduction follows  $O_2$  on the redox ladder (Fig. 10), resulting in the production of  $N_2O$  or  $N_2$  via denitrification, or  $NH_4^+$  via dissimilatory  $NO_3^-$  reduction (DNRA). Iron reduction occupies the middle of the redox ladder, while methanogenesis under the lowest redox conditions (Fig. 10). Below we review the redox-sensitive biogeochemical cycles of N, Fe, and C, which are particularly important in humid tropical forests and have been studied along the LEF elevation gradient. We also briefly review patterns in P cycling along the elevation gradient. Although P is not directly affected by redox dynamics, the intimate relationship among Fe and P cycles results in significant indirect effects of redox on soil P pools.

### Nitrogen cycling

The N-rich soils typical of highly weathered tropical forests are somewhat of an enigma given the multitude of N loss pathways in these ecosystems (Vitousek and Howarth 1991), particularly under fluctuating redox conditions. Most N cycling pathways are sensitive to redox. Ammonification occurs under both oxic and anoxic conditions, but  $NH_4^+$  oxidation to  $NO_2^-$  and  $NO_3^-$  is generally assumed

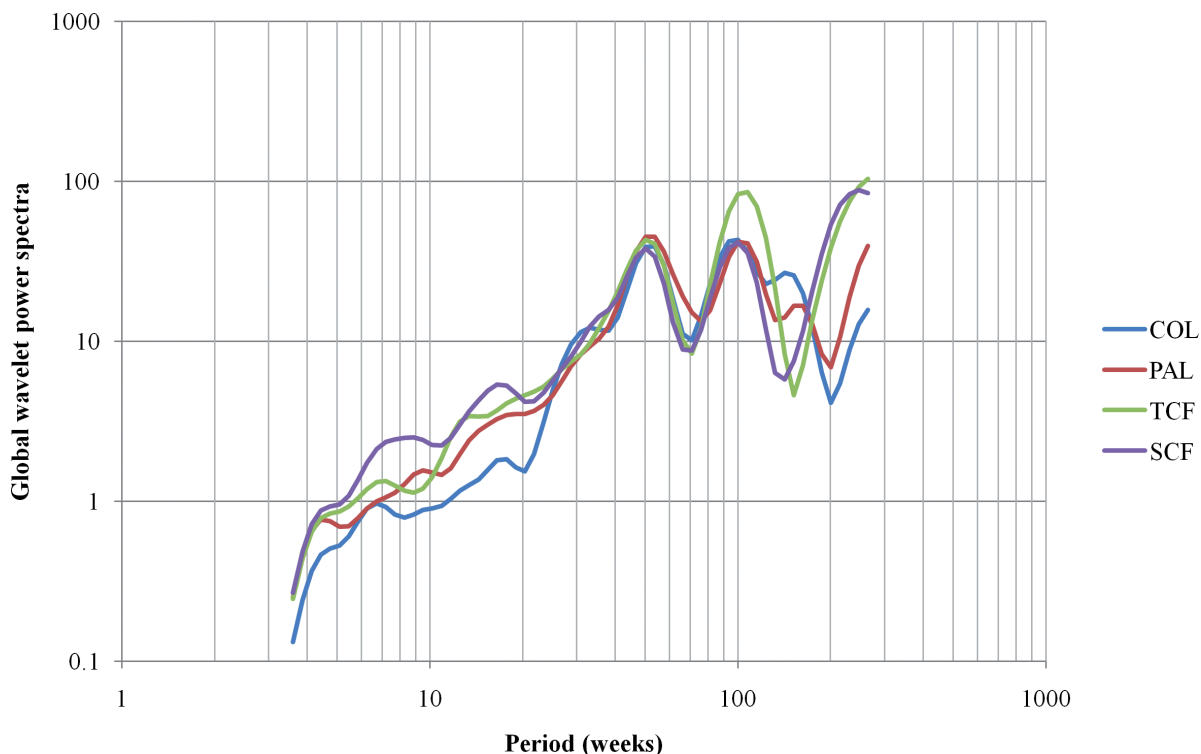


Figure 6. Global wavelet power spectra for the soil  $O_2$  time series. The lines represent the power of the spectra at a range of periodicities for the average soil  $O_2$  in each forest. The strongest periodicities for all four forest types were at annual time scales.

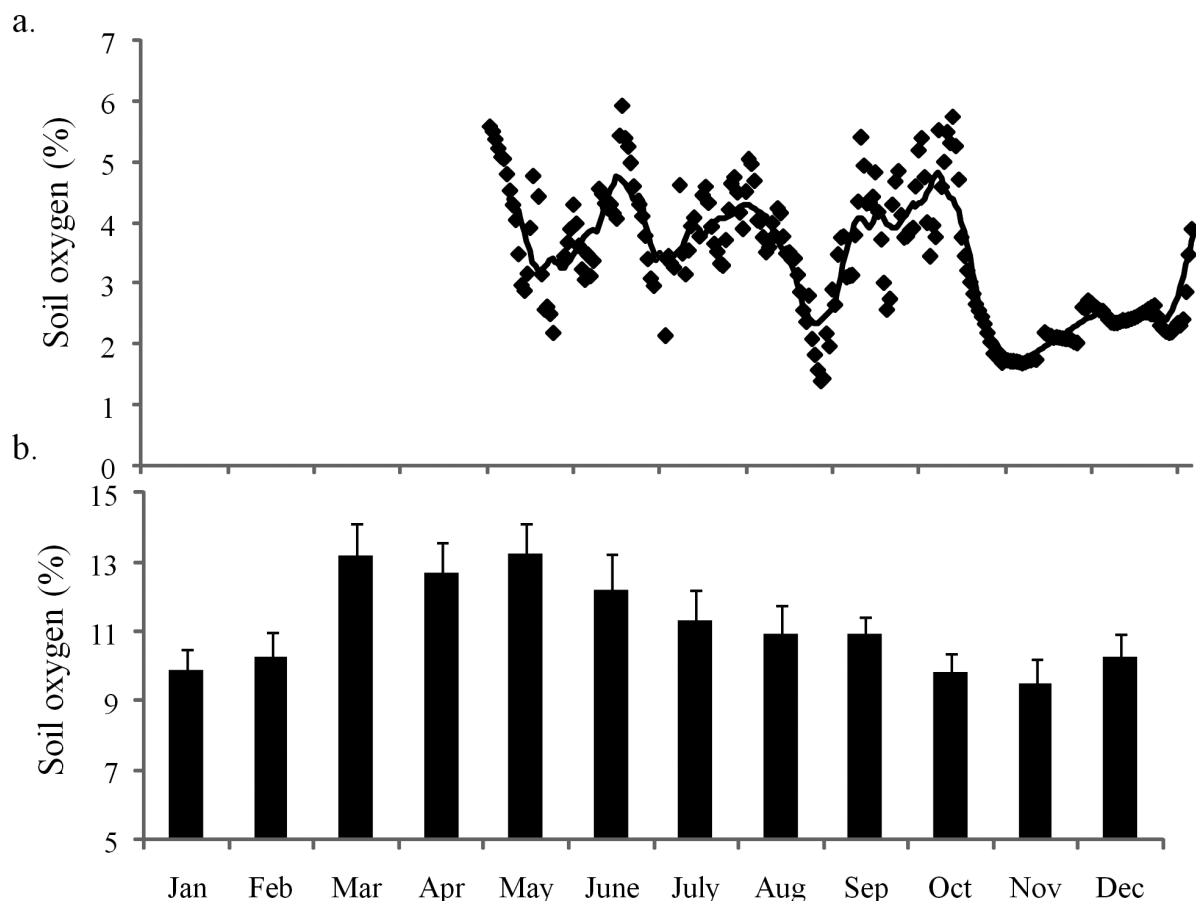


Figure 7. (a) Daily means of hourly soil oxygen measurements from a TCF site at 930 m a.s.l. with the solid line representing a 2 week centered moving average (data from Liptzin et al. 2011). (b) The monthly averages of soil O<sub>2</sub> in the TCF forest. The mean was calculated using the smoothed data (3 month centered moving average) of the three TCF plots.

to be strictly an aerobic process. Recent work in oceans, wetlands, and tropical forests is challenging this notion by suggesting that reduction of Fe and Mn oxides could be coupled with the oxidation of  $\text{NH}_4^+$  to form  $\text{NO}_2^-$  (Clement et al. 2005),  $\text{NO}_3^-$ , or N gases (Yang et al. pers. comm.). Anammox, anaerobic  $\text{NH}_4^+$  oxidation coupled to  $\text{NO}_2^-$  reduction to produce  $\text{N}_2$  has been documented in ocean sediments (Dalsgaard and Thamdrup 2002), but not in terrestrial soils. Low redox conditions in C-rich soils can stimulate both N losses via denitrification (Groffman and Tiedje 1989) and N retention via DNRA (Silver et al. 2001, 2005, Templer et al. 2008).

Both net and gross N cycling have been measured along the LEF elevation gradient. Gross N mineralization and nitrification rates were significantly higher in the colorado, palm and cloud forest types relative to the lower elevation tabonuco forest in the LEF (Silver et al. 2001, 2010). Net N mineralization rates ranged from  $-2.1 \pm 0.7$  to  $6.0 \pm 5.5 \mu\text{g g}^{-1} \text{d}^{-1}$  in the 12 plots of the elevation gradient, but there were no statistically

significant trends with elevation (Silver et al. 2010). Net nitrification rates differed significantly within and across forest types, but also followed no distinct pattern with elevation (Silver et al. 2010). The lack of a strong pattern in net and gross N cycling is likely a result of the complex suite of variables that affect mineral N production and consumption. While soil O<sub>2</sub> availability is an important driver of N cycling rates, the non-linear dynamics of redox and interactions with labile C pools and other soil properties (e.g. pH, total N pools) likely contribute to the variability observed.

Nitrate can be quickly reduced during short term anaerobic events or in anaerobic microsites via denitrification or DNRA. Denitrification is the reduction of  $\text{NO}_3^-$  to  $\text{N}_2\text{O}$  and  $\text{N}_2$  gas under anaerobic conditions. Tropical forests are the largest natural source of  $\text{N}_2\text{O}$  globally (Bouwman et al. 1995), however,  $\text{N}_2\text{O}$  fluxes were generally low in cloud, colorado and palm forest, possibly due to complete denitrification to  $\text{N}_2$  under strongly reducing conditions as well as low standing  $\text{NO}_3^-$  pools (Firestone

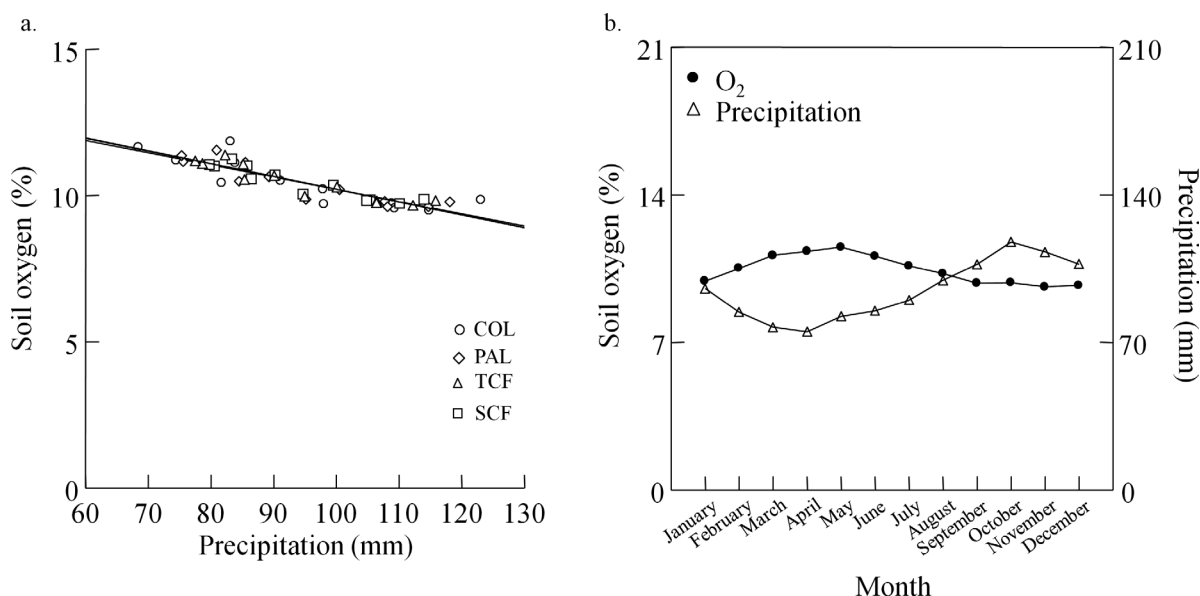


Figure 8. The relationship of monthly soil O<sub>2</sub> and precipitation. Data were smoothed using 3-month running averages. (a) Monthly precipitation plotted against average monthly soil O<sub>2</sub> by forest type. (b) Monthly soil O<sub>2</sub> and total monthly precipitation averaged across all forest types.

et al. 1980). DNRA requires similar conditions as denitrification: labile C, NO<sub>3</sub><sup>-</sup>, and anoxia. However, DNRA may be favored under lower redox conditions than denitrification (Tiedje et al. 1982). In laboratory experiments, DNRA rates generally decreased in soils from tabonuco to palm to cloud forest under ambient atmospheres, and palm forest soils had the greatest DNRA potentials under an anaerobic atmosphere (Silver et al. 2001). DNRA is likely favored over denitrification under strongly reducing conditions, and had the potential to consume the NO<sub>3</sub><sup>-</sup> pool and limit denitrification rates. This is likely to contribute to N retention in ecosystems. Templer et al. (2008) reported that DNRA rates were equivalent to up to 25% of gross mineralization in the colorado forest and were a stronger sink for NO<sub>3</sub><sup>-</sup> than either N<sub>2</sub>O production or leaching losses.

### Iron redox biogeochemistry

Iron is the most abundant redox-active metal on earth, and much of the tropical forest biome is underlain by highly weather soils rich in Fe minerals (Sanchez 1977). Most Fe redox reactions in natural soils and sediments are microbially mediated (Lovley and Phillips 1986, Roden and Wetzel 1996, Frenzel et al. 1999, Ratering and Schnell 2000) and Fe reducing and oxidizing microbes are abundant in tropical forest soils. In the LEF, Fe reducers alone amounted to ca  $1.2 \times 10^9$  cells, or approximately 6% of the total number of microbial cells in the soil (Dubinsky et

al. 2010). Fluctuating redox conditions drive high rates of Fe-redox cycling in humid tropical forest soils (DeAngelis et al. 2010). During Fe reduction, Fe(III) becomes an electron acceptor for anaerobic respiration, producing Fe(II) and CO<sub>2</sub> while consuming organic C. During microbial Fe(II) oxidation the process is reversed consuming C and producing Fe(III). The rapidity of these Fe-redox reactions, occurring on the scale of hours to days (Chacon et al. 2006, Liptzin and Silver 2009), results in considerable energy transfer and can drive a significant amount of C cycling. Iron cycling associated with fluctuating redox can also alter the crystallinity of Fe minerals and potentially alter the sorption and reactivity of the resulting minerals (Thompson et al. 2006).

Dubinsky et al. (2010) measured greater total Fe concentrations in the lower elevation forests (31–58 mg Fe g<sup>-1</sup>) than in the upper elevations (18–22 mg Fe g<sup>-1</sup>). Poorly crystalline Fe minerals were a relatively small proportion of the total Fe pool (6–11 mg Fe g<sup>-1</sup>) and generally followed the opposite trend with elevation. Rates of Fe reduction increased with elevation, likely as a function of more frequent intermediate to low redox events and abundant labile C pools (McGroddy and Silver 2000, Chacon et al. 2006). The relative proportion of Fe(III) reducers increased with elevation from 0.7 (± 0.3) to 5.7 (± 1.0) % of total cells and was significantly positively correlated with the rate of Fe(II) production (Dubinsky et al. 2010). Iron reduction can account for a significant amount of anaerobic C respiration. In a lower elevation forest (350 m a.s.l.) Liptzin and Silver (2009) reported C oxidation rates of 0.1 to 1.4 μg

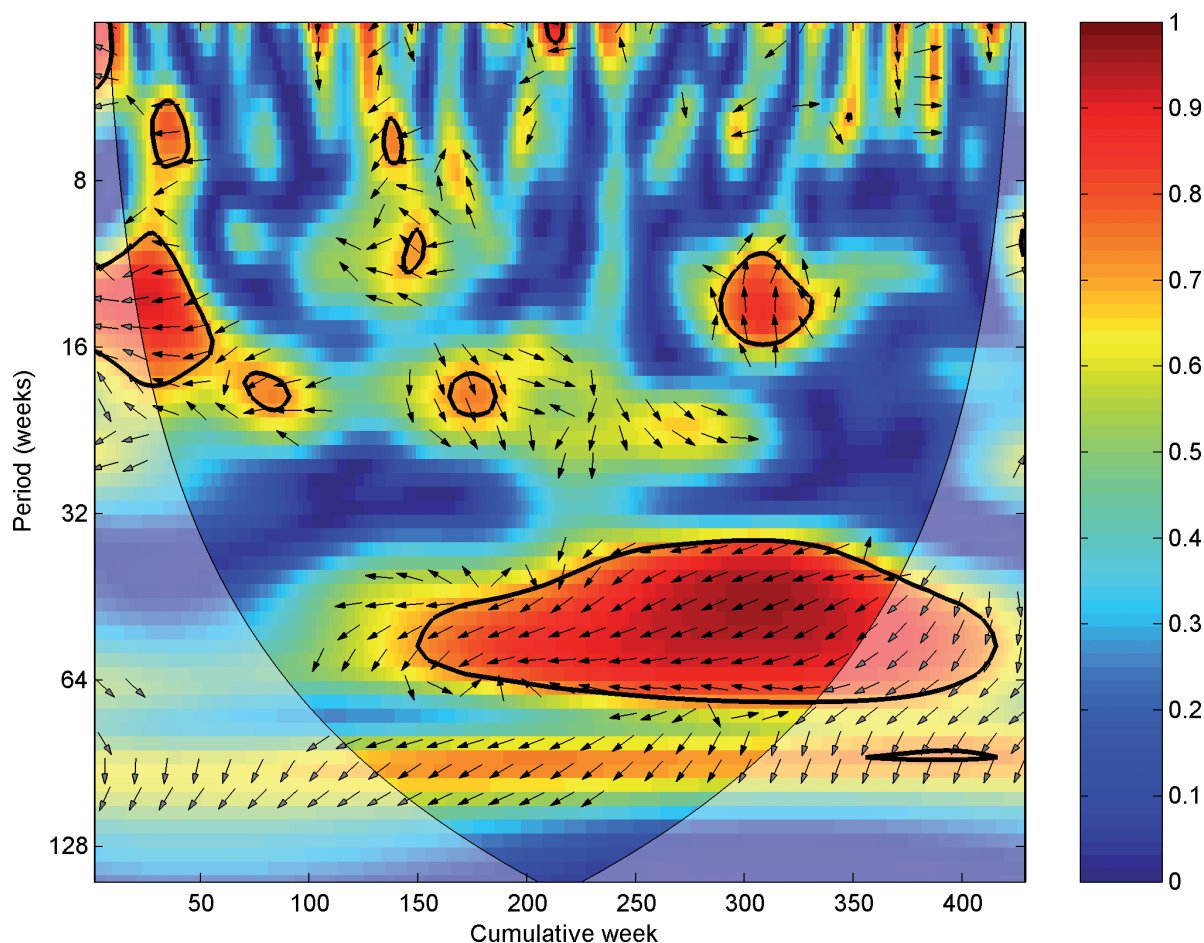


Figure 9. Wavelet coherence analysis and phase difference between average soil  $O_2$  and the 2 week precipitation totals in the TCF for the entire study period, 1994–2002. The phase difference between the two time series is indicated by arrows: in-phase pointing right (i.e. no lags between time series) and anti-phase pointing left. The color codes for power values of the WC are from dark blue (low values) to dark red (high values). Thick black contour lines represent significant (5%) WC. The semi-transparent region below the thin black line indicates the cone of influence, which delimits the region influenced by edge effects.

$C\ g^{-1}\ soil\ d^{-1}$ . Based on the stoichiometry of Fe(III) reduction, C oxidation associated with Fe(II) production alone accounted for 4 to 7% of total  $CO_2$  production in the lower elevation forest to 44% of soil  $CO_2$  production in the upper elevation cloud forest (Liptzin and Silver 2009, Dubinsky et al. 2010).

Oxides and hydroxides of Fe can form strong chemical bonds with P in soils. This bonding is thought to be the primary factor limiting P availability to biota in tropical forests (Vitousek and Sanford 1986). As soil  $O_2$  declines, reductive Fe dissolution can release Fe-bound P into the soil solution. This P can be utilized by plants or microbes, or be leached to deeper soil horizons or from the system in water export (McGroddy and Silver 2000, McGroddy et al. 2008). In the LEF total soil P decreased with elevation and was positively correlated with temperature and negatively correlated with soil moisture (McGroddy and

Silver 2000). Similar results have been found in Hawaii (Miller et al. 2001) and have been linked with increasing soil reduction and the dissolution of Fe oxyhydroxides, enhancing the solubility of P (Liptzin and Silver 2009). Soil Fe pools in the LEF were strongly positively correlated with total P along the elevation gradient (McGroddy and Silver 2000). Soil P can be fractionated in the laboratory to identify pools that are likely to react with Ca, Fe, and Al or originate as organic P (Tiessen and Moir 1993). In the LEF, the more strongly sorbed P pools extracted in 1M HCl and concentrated HCl were proportionally greater in the upper elevation soils (McGroddy and Silver 2000), suggesting that Ca- and organic bound P pools became important for P retention in these humid environments. The amount of Ca-bound P was greatest in the upper elevation soils, and was indicative of the relatively high Ca pools and higher pH of these soils (Silver et al.

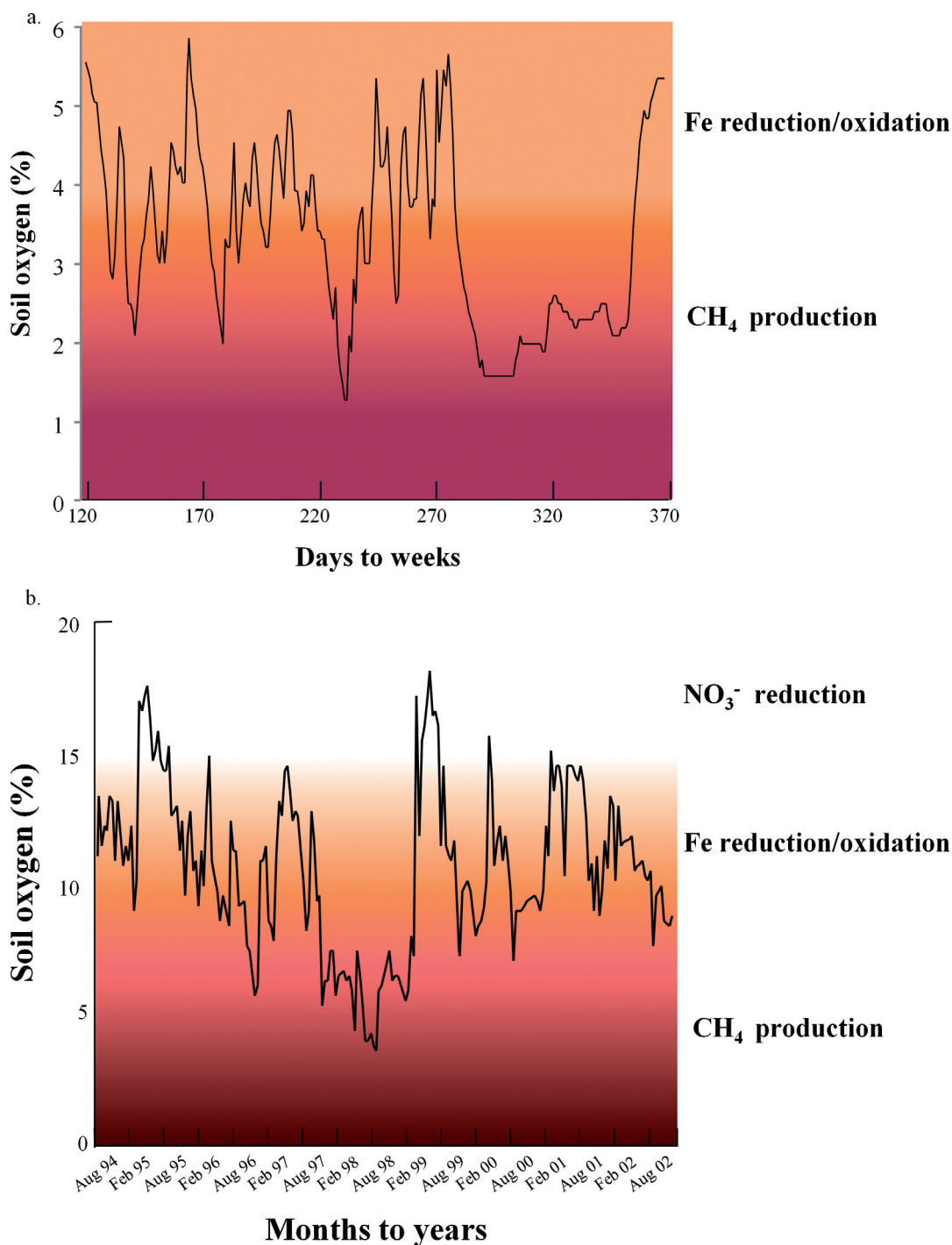


Figure 10. Conceptual model linking periodicity in soil O<sub>2</sub> with some key redox sensitive biogeochemical processes at temporal scales of days to weeks (a) and months to years (b). The solid line in (a) highlights short term fluctuations in daily mean soil O<sub>2</sub> data from a tall cloud forest site (data from Liptzin et al. 2011). Both the rapid changes over a period of days as well as the periodic fluctuations at ~2 week intervals are evident. The solid line in (b) highlights the seasonal pattern of soil O<sub>2</sub> based on the 8 yr of data from the tall cloud forest from the present study. Even though precipitation occurs year round at this site, there is still a strong seasonal signal as well as interannual variability in soil O<sub>2</sub> related to differences in the magnitude of precipitation. Colors in both panels highlight the frequency and duration of periods at the various temporal scales when key redox-sensitive N, Fe, and C transformations are likely to dominate the redox reactions.

1994, Olander et al. 1998). A recent study documented significant P inputs in dust to soils of the LEF (Pett-Ridge 2009), potentially contributing to the large Fe, Al, and Ca bound P pools.

## Carbon cycling

Carbon tends to cycle rapidly in humid tropical forests. These ecosystems are generally characterized by high net primary productivity (Del Grosso et al. 2008) coupled with rapid rates of decomposition (Parton and Silver et al. 2007). Decomposition tends to decrease in low redox soils, leading to the buildup of soil organic matter (Day and Megonigal 1993, Schuur et al. 2001). Net primary production generally declines along the LEF elevation gradient (Weaver and Murphy 1990) and soil organic matter increases, although the patterns are not always linear (Silver et al. 1999, McGroddy and Silver 2000). For example, McGroddy and Silver (2000) found that soil C pools were greatest and soil respiration rates were lowest at 1000 m a.s.l., but that colorado forest at 800 m a.s.l. had lower soil C pools, lower root biomass, and lower forest floor C concentrations than the same cover type at 650 m a.s.l. Forests at 800 m a.s.l. also had the highest rates of soil respiration, which likely contributed to the relatively small C pool sizes. These data highlight the inherent spatial heterogeneity within and across these complex ecosystems.

Tropical forests are an important source of atmospheric CH<sub>4</sub> (Fung et al. 1991, Silver et al. 1999, Fletcher et al. 2004, Frankenberg et al. 2005, 2006, Teh et al. 2005). Methanogenesis requires anaerobic conditions, thus providing additional evidence of the abundance of anaerobic microsites in tropical soils. Soils in the LEF have the potential to produce large amounts of methane. Silver et al. (1999) measured soil CH<sub>4</sub> concentrations (0–10 cm depth) of up to  $2.4 \times 10^5$  ppmv in the short cloud forest (968 m a.s.l.), and net positive fluxes in the cloud and colorado forest types along the elevation gradient. The balance between CH<sub>4</sub> production and consumption will determine the net flux of CH<sub>4</sub> to the atmosphere. Soils from the lower elevations of the upper montane gradient (600–650 m a.s.l.) generally consumed most of the CH<sub>4</sub> produced leading to a weak positive flux or equilibrium with the atmosphere (Teh et al. 2005). The same study showed strong net production in the short cloud forest (1000 m a.s.l.), equivalent to fluxes reported from wetland soils (Sass and Fisher 1997, Mosier et al. 1998).

Net fluxes underestimate total CH<sub>4</sub> production in the LEF; <sup>13</sup>C tracer studies indicated that 48–78% of the methane produced was oxidized before reaching the atmosphere. Surprisingly, this and a related study showed that CH<sub>4</sub> production was relatively insensitive to bulk soil O<sub>2</sub> concentrations in both the colorado and cloud forests, indicating that anaerobic microsites are well protected

from O<sub>2</sub> intrusion, likely by well-aggregated soils (Teh et al. 2005, 2006).

## Summary and conclusions

Our results show that soils of the LEF elevation gradient experienced rapid fluctuations in O<sub>2</sub> availability, likely tied to the timing of rainfall events, and also fluctuated seasonally in relation to the amount of precipitation. This latter trend was a surprising result; these ecosystems are generally considered to be aseasonal with regard to climate. While soil O<sub>2</sub> concentrations were dynamic in time and space, they did not follow strong linear trends with elevation. Soils in the colorado forest, the lower end of our gradient, had the highest redox potential. These patterns are likely driven by differences in soil bulk density along the gradient, which in turn is linked to soil C pools. The lack of difference among the palm, tall, and short cloud forests was also a surprising result and indicates that simple relationships do not exist between soil redox dynamics and plant community structure and NPP.

Our conceptual model provides a framework for exploring patterns in N, Fe, and C cycling in tropical forest soils with fluctuating redox. The patterns observed provide potential explanations for the relatively low N<sub>2</sub>O production potential, despite relatively high rates of gross N mineralization. The dynamic redox in the upper LEF soils stimulated considerable Fe redox cycling and supported a large associated microbial community (Dubinsky et al. 2010). Iron pools and microbial communities followed clear trends with elevation, likely linked with the general increase in soil C along the gradient (McGroddy and Silver 2000). Iron redox cycling was tightly coupled with the C cycle, and with P availability in these soils (Liptzin and Silver 2009). Finally, soils of the LEF have considerable CH<sub>4</sub> production potential, although CH<sub>4</sub> oxidation at the surface decreases the net flux to the atmosphere.

The data presented and reviewed here provide a picture of soils along montane elevation gradients as dynamic environments responding to the timing of rainfall on short temporal scales and the magnitude of rainfall at longer time scales. The tight temporal coupling of soil O<sub>2</sub> concentrations and rainfall suggest that these ecosystems are likely to be very sensitive to climate change. Shifts in the timing and amount of rainfall are likely to alter redox dynamics, nutrient retention and loss, and greenhouse gas emissions. Future research should explore both direct and indirect effects of precipitation change on soil redox dynamics, plant ecology, and biogeochemical cycling.

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