ECOSYSTEMS

Temporal Dynamics in Soil Oxygen and Greenhouse Gases in Two Humid Tropical Forests

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ABSTRACT

Soil redox plays a key role in regulating biogeochemical transformations in terrestrial ecosystems, but the temporal and spatial patterns in redox and associated controls within and across ecosystems are poorly understood. Upland humid tropical forest soils may be particularly prone to fluctuating redox as abundant rainfall limits oxygen (O_2) diffusion through finely textured soils and high biological activity enhances O_2 consumption. We used soil equilibration chambers equipped with automated sensors to determine the temporal variability in soil oxygen concentrations in two humid tropical forests with different climate regimes. We also measured soil trace gases (CO_2, N_2O, and CH_4) as indices of redox-sensitive biogeochemistry. On average, the upper elevation cloud forest had significantly lower O_2 concentrations ($3.0 \pm 0.8\%$) compared to the lower elevation wet tropical forest ($7.9 \pm 1.1\%$). Soil O_2 was dynamic, especially in the wet tropical forest, where concentrations changed as much as 10% in a single day. The periodicity in the O_2 time series at this site was strongest at 16 day intervals and was associated with the hourly precipitation. Greenhouse gas concentrations differed significantly between sites, but the relationships with soil O_2 were consistent: O_2 was negatively related to both CO_2 and CH_4 and positively related to N_2O. These results are among the first to quantify the temporal and spatial scale of variability in soil redox in humid tropical forests, and show that the timing of precipitation plays a strong role in biogeochemical cycling on the scale of hours to weeks.

Key words: soil oxygen; greenhouse gases; tropical forests; soil redox; biogeochemical cycling; wavelet analysis.

INTRODUCTION

Oxygen (O_2) is a fundamental driver of biogeochemical cycling on Earth. Oxygen concentrations are intimately tied to carbon (C) fixation and oxidation, and are an important driver of the anti-

phase fluctuations of O_2 and carbon dioxide (CO_2) in the atmosphere at annual time scales (Keeling and Severinghaus 2000). Oxygen, by its control of redox potential, influences a considerable proportion of nutrient cycles as well. Some elements (for example, nitrogen (N), sulfur (S), iron (Fe), manganese (Mn)) have multiple redox states. Other elements such as phosphorus are only indirectly related to redox state through its interactions with redox-active elements, especially Fe (Baldwin and Mitchell 2000). The contemporary surface of Earth is a highly oxidizing environment. However, reducing conditions exist in

soils, sediments, and water columns. Key biogeochemical pathways, mediated by microbial processes associated with C oxidation, occur in these anoxic environments.

The greenhouse gases CO_2, nitrous oxide (N_2O) and methane (CH_4) are produced and consumed in soils via redox reactions. Carbon oxidation produces CO_2 as a byproduct of aerobic respiration, or as the product of anaerobic respiration or fermentation. For example, Fe and Mn reduction can be coupled to C oxidation in the absence of O_2, producing CO_2 (Lovley 1991; Ponnamperuma 1972). Denitrification represents the major loss pathway of reactive N from the biosphere to the atmosphere converting nitrate to unreactive dinitrogen gas or nitrous oxide (N_2O) under anaerobic conditions (Seitzinger and others 2006). Methanogenesis is also an important redox-sensitive process as either CO_2 or simple organic compounds are reduced to methane (CH_4) under anaerobic conditions.

Most of the research on redox dynamics has been conducted in wetlands, water columns, and aquatic sediments which can experience near constant anoxic conditions for months to years. Upland soils can also experience low redox, but unlike aquatic systems, redox tends to fluctuate in soils, both spatially and temporally (Silver and others 1999; Schuur and Matson 2001). Despite the fact that abundant evidence exists for redox-active biogeochemical cycling in upland soils, the links between O_2 concentrations and biogeochemically relevant redox reactions are poorly understood in these environments. Oxygen can be rapidly consumed in some finely textured soils faster that it can be resupplied via diffusion, leading to low redox conditions. Within soil aggregates, O_2 concentrations can decrease from oxic to anoxic over a distance of millimeters (Sexstone and others 1985).

Redox dynamics may be particularly important where warm, wet conditions, finely textured soils, and high biological activity increase the likelihood of anoxic events. Warm temperatures stimulate biological activity and decrease the solubility of O_2 in water (Weiss 1970). High rainfall typical of the humid tropics leads to periods of high water content (for example, Cleveland and Townsend 2006). Tropical soils are predominantly oxisols and ultisols which tend to be clay-rich with high water-holding capacity (Vitousek and Sanford 1986). This combination may lead to periods when the O_2 demand outpaces the supply driving down bulk soil O_2 concentrations. Redox dynamics in these soils have been shown to affect the cycling of N, Fe, and P (via Fe reduction and oxidation), as well as microbial community composition and activity (Silver and

others 2001, 2005; Chacon and others 2006; Thompson and others 2006; Peretyazhko and Sposito 2005; Pett-Ridge and others 2006; Liptzin and Silver 2009; Dubinsky and others 2010; DeAngelis and others 2010). Tropical forest soils are well documented sources of CO_2, N_2O, and CH_4 (Keller and others 1986; Teh and others 2005; Frankenberg and others 2008; Melillo and others 2001; Vitousek and Matson 1992). However, the temporal scale of redox fluctuations and spatial heterogeneity in the redox environment are not well documented in these ecosystems. Furthermore, the relationships between fluctuations in soil O_2 concentrations, a proxy for fluctuating redox, and greenhouse gas concentrations in soils is poorly understood.

The goals of this study were to explore the spatial and temporal patterns in soil O_2 concentrations and examine the relationships with precipitation and temperature as climatic drivers. We chose two sites at opposite ends of an elevational climate gradient in Puerto Rico to make, to our knowledge, the first continuous (hourly) O_2 measurements in upland soils. We also determined the relationship of O_2 with CO_2, N_2O, and CH_4 concentrations as a first approximation of the dynamic relationships among these key atmospheric gases.

MATERIALS AND METHODS

Study Area

This study was conducted in two forest types within the Luquillo Experimental Forest in northeastern Puerto Rico (Lat. 18° 18′N; Long. 65° 50′W), part of the NSF-sponsored Long Term Ecological Research Program. The lower elevation site (350 m asl) was located in the Bisley Research Watersheds and occurs within lower montane wet tropical (*Tabonuco*) forest type. The upper elevation site (930 m asl) was located in the cloud forest zone. These sites represent the lowermost and uppermost primary forest types along an elevation gradient of plant communities in Luquillo (Table 1; Brown and others 1983). The two study sites were located on relatively level topography. Both sites occur on highly weathered soils derived from volcaniclastic sediments: in Bisley the soils are ultisols and oxisols in the Cristal/Humatus/Zarzal complex whereas in the cloud forest the soils are classified as an inceptic Hapludox (oxisols, USDA NRCS 2002; Scatena 1989). Precipitation is relatively evenly distributed throughout the year (>200 mm/month) and increases from 3500 to 5000 mm y^{-1} from Bisley to the cloud forest; mean annual temperature

Table 1. Site Characteristics with Standard Errors in Parentheses

	Bisley	Cloud Forest
Life zone	Subtropical wet	Lower Montane rain
Forest type	Tabonuco	Cloud
Air temperature (°C)	21	19
Precipitation (mm)	3500	5000
Total soil C (%)	3.1 (0.07)	16.0 (0.05)
Total soil nitrogen (%)	0.27 (0.005)	0.70 (0.027)
Soil pH	5.0 (0.03)	4.7 (0.08)

Climate data are from Brown and others (1983) and Weaver and Murphy (1990).

decreases slightly with the altitude from 21°C at Bisley to 19°C in the cloud forest with little variability within sites throughout the year (Brown and others 1983; Weaver 1994).

Field and Laboratory Methods

Soil equilibration chambers were placed in the ground typically from 0.5 to 1 m from the nearest neighboring chamber. At the Bisley site, 14 chambers were located within an area of approximately 50 m^2, whereas in the cloud forest site, the 15 chambers were installed over a larger area (~100 m^2) to avoid dense surficial roots. The chambers were 15 cm long and constructed of 5 cm diameter polyvinyl chloride (PVC) pipe, open on the bottom and capped on top. To insert the chambers, 10 cm of soil was removed with a metal corer of similar diameter and chambers were pushed into the hole an additional 5 cm so that the cap was just below the soil surface. Thus, the chambers contained 10 cm of headspace over 5 cm of soil. Oxygen sensors (Apogee Instruments, Logan, UT) were suspended inside the headspace of the chambers. The chamber tops were fitted with copper tubing with a three-way stopcock for trace gas sampling. Cable and tubing connections were thoroughly coated with automotive Goop (Eclectic Products, Eugene, OR) to create an airtight seal. The removed soil was used to backfill the small gap between the chamber and the surrounding intact soil. The chambers were sampled for 5 months in Bisley and 9 months in the cloud forest. The time period allowed for sufficient replication of within-site temporal variability in soil O_2 concentrations needed to identify trends in both sites. To collect samples for trace gas (CO_2, CH_4, and N_2O) analysis, a 30-ml sample was extracted from the chamber with a polypropylene syringe and injected into a sealed, pre-evacuated 20 ml Wheaton vial. Soil O_2

data were collected hourly using a data logger (CR1000) and multiplexer (AM16/32) (Campbell Scientific, Logan, UT). Trace gas sampling occurred weekly in Bisley ($n = 8$) and approximately biweekly ($n = 19$) in the cloud forest.

The chambers were allowed to equilibrate with the surrounding soil atmosphere. In Bisley, this process lasted only a few days for most sensors. Average soil O_2 concentrations were much lower in the cloud forest and for almost half of the chambers, soil O_2 decreased over 3–4 weeks (polynomial fit $R^2 > 0.9$) before reaching equilibration. The measurements during this transitory period were excluded in subsequent analyses. In Bisley, an additional gap of a week was due to a battery failure. In the cloud forest site, O_2 concentrations were occasionally observed to change following trace gas sampling, typically an increase of less than 1% oxygen. All the chambers were affected at least once during the sampling, but some chambers were more susceptible than others. The data when affected by trace gas sampling were removed from the analysis until the signal re-equilibrated, typically from 1 to 3 days.

Data Analysis

Differences in gas concentrations among sites were tested with one-way analysis of variance (ANOVA) with mean values from the individual chambers as replicates. Relationships among gas concentrations were examined with correlation and regression analyses with individual samples from chambers as replicates. Data were log transformed as needed to meet the distributional requirements of the statistical tests. Wavelet analysis was performed to explore the temporal variability of O_2 time series and their relationship with climate drivers. This spectral technique, analogous to Fourier analysis, breaks up the process variance into pieces, each of which represents the contribution on a particular scale (Cazelles and others 2008). The wavelet transformation of a discrete signal x_n (or hits n-order stationary increment) of length N recorded at δt interval, is defined as the convolution integral (Lau and Weng 1995; Torrence and Compo 1998):

$$W_n(s) = \left(\frac{\delta t}{s}\right)^{1/2} \sum_{n'=0}^{N-1} x_{n'} \, \psi_0^* \left(\frac{n - n'}{s/\delta t}\right) \quad (1)$$

where ψ_0^* is the complex conjugate of the scaled and translated mother wavelet, and s is the wavelet scale at which the transformation is applied. The continuous wavelet transformation is calculated by continuously shifting the scale and time in

equation (1). The wavelet power spectrum (WPS), is then computed as $WPS_n(s) = W_n(s)W_n^*(s)$. Analogously, the wavelet co-spectrum (WCS) between two time series x_n and y_n is defined as $WCS_n^{x,y}(s) = W_n^x(s)W_n^{y*}(s)$. The global wavelet power spectra, the analog of Fourier spectra, are the time average of WPS (or WCS):

$$S_{xx}(s) = \frac{1}{n}\sum_{n=1}^{n} WPS_n^x(s)$$

$$S_{xy}(s) = \frac{1}{n}\sum_{n=1}^{n} WCS_n^{x,y}(s)$$

These quantities can be combined to form the wavelet magnitude square coherence, or simply wavelet coherence WC:

$$WC = \frac{\left|\langle S_{xy}\rangle\right|^2}{\langle S_{xx}\rangle\langle S_{yy}\rangle} \tag{2}$$

where the angular brackets indicate ensemble averages if multiple realizations of x or y are available. WC can be thought of as the spectral correlation between two time series and, equivalent to the R^2, can vary between 0 and 1. Importantly, WC finds regions in the frequency space where two time series co-vary, but do not necessarily have high common power (Cazelles and others 2008; Grinsted and others 2004; Yates and others 2007). The use of a complex wavelet in this analysis also allows for exploration of the phase difference between the two time series evaluated as $\tan^{-1}[\Im\{WCS^{xy}(s)\}/\Re\{WCS^{xy}(s)\}]$.

The hourly O_2 series were numerically differentiated ($dO_t = O_t - O_{t-1}$) to reduce non-stationarity. Physically, these differences represent the time series of O_2 losses or gains by the soil in 1 h time intervals. The hourly climate (temperature and precipitation) data for the two sites were provided by the LTER and USDA Forest Service long-term climate monitoring program (F. Scatena for Bisley and W. Silver for cloud forest, available at http://luq.lternet.edu/data). For Bisley all the O_2 chambers were used in this analysis. For the cloud forest chambers with many missing data were excluded ($n = 3$), as were chambers with little temporal fluctuation over the study period, yielding a sample size of five chambers. Thus, the time series evaluated at the cloud forest site were only from the chambers sensitive to environmental fluctuation and may not be indicative of how the entire site responds to climate. A 95% confidence level for the WC was obtained through Monte Carlo Simulation using 1,000 surrogates (Palus 2008).

RESULTS

The mean O_2 concentration in Bisley (7.9 ± 1.1%) was significantly higher than in the cloud forest (3.0 ± 0.8%) ($F_{1,27} = 9.2$, $P = 0.005$). In Bisley, the chambers varied in O_2 concentrations over time and space with some relatively oxic, and some relatively anoxic, but about half experienced an almost equal probability of O_2 concentrations from 0–19% (Figure 1A). In the cloud forest, in contrast, most of the chambers were relatively anoxic, as nine of the 15 sensors remained below 1% O_2 the entire sampling period (Figure 1B). The distribution of hourly measurements in the cloud forest site was strongly skewed to anoxic conditions, with soil O_2 concentrations less than 1% almost 60% of the measurement period (Figure 2). In contrast, the overall distribution of soil O_2 across sensors over time was strikingly uniform.
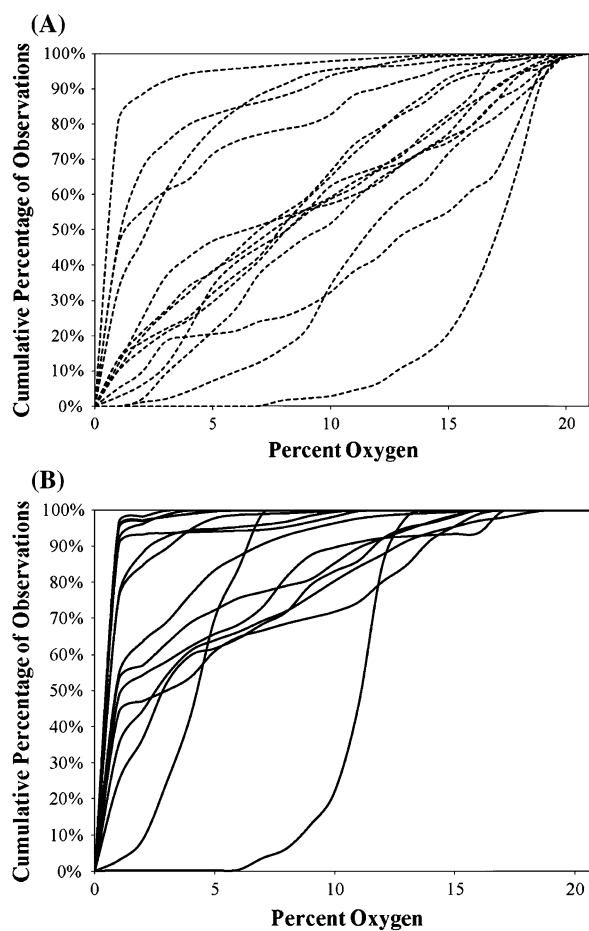

Figure 1. The cumulative percent of observations of soil O_2 concentrations ranging from 0–21% from buried equilibration chambers in Bisley (**A**) and the cloud forest sites (**B**).
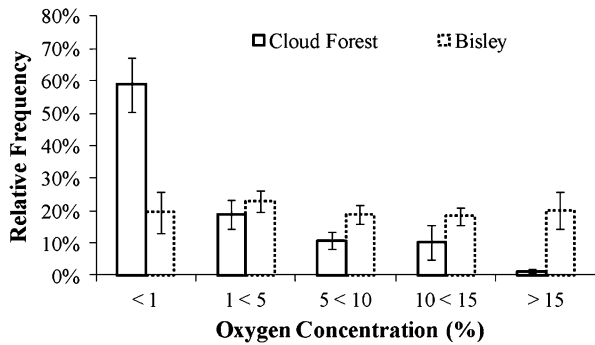
Figure 2. Relative frequency of hourly soil O_2 concentrations in buried soil equilibration chambers in Bisley and the cloud forest sites.

The global WPS for O_2 suggested periodicity in O_2 concentration of 8 to 60 days, with a prominent peak located at 16 days at Bisley. The chambers that fluctuated in the cloud forest showed a broader energetic band at periods greater than 7 days. The global WPS for precipitation exhibited periodicity between 3 and 30 day periods, with considerable energy at lower frequencies (more evident in the longer record at the cloud forest site). At higher frequencies, the precipitation and O_2 spectra had similar power law decay at both sites (Figure 3A). The prominent peak for the temperature spectrum, occurring at a period of 1 day, was absent from the O_2 and precipitation spectra. These results suggest that precipitation, more than temperature, may be responsible for the temporal dynamics of soil O_2.

Based on the similarities in the spectra, we examined the WC between the O_2 and precipitation time series (Figure 4). At the Bisley site, there was significant coherence (0.25–0.35) in the region of maximum energy for O_2, at periods of 4–25 days. The average phase difference was $-153°$ for periods of 3–20 days, indicating that an increase of precipitation corresponded to a decrease in O_2. The approximately antiphase relationship of the two time series resulted in increases in O_2 concentrations during rain-free days with an inflection point after a rainfall event and decreases in O_2 concentrations during wet periods with the trough in the O_2 time series occurring when the rainfall ceased. For example, a 12 day fluctuation involved a 5-day dry period with increasing O_2 concentrations, followed by a 7-day wet period with declining O_2 concentrations.

Several time periods with more than 4 consecutive dry (<1 mm rainfall) days occurred during the sampling period in Bisley. For example, during the dry period from DOY 88–93, essentially all of the sensors increased in O_2 with almost simultaneous inflection points when a rain event occurred on DOY 93 (Figure 5A). There were fewer instances of long dry periods in the cloud forest, and the coherence between O_2 and precipitation was only significant at periods of about 2 days. The only dry period longer than 4 days in length during the measurement period in the cloud forest was associated with increases in O_2 in only four of the sensors (Figure 5B). In general, there were more dry days and the dry periods persisted longer in Bisley compared to the cloud forest site (Table 2). The longest dry period during 2007–2008 lasted for 12 days and occurred at both sites.
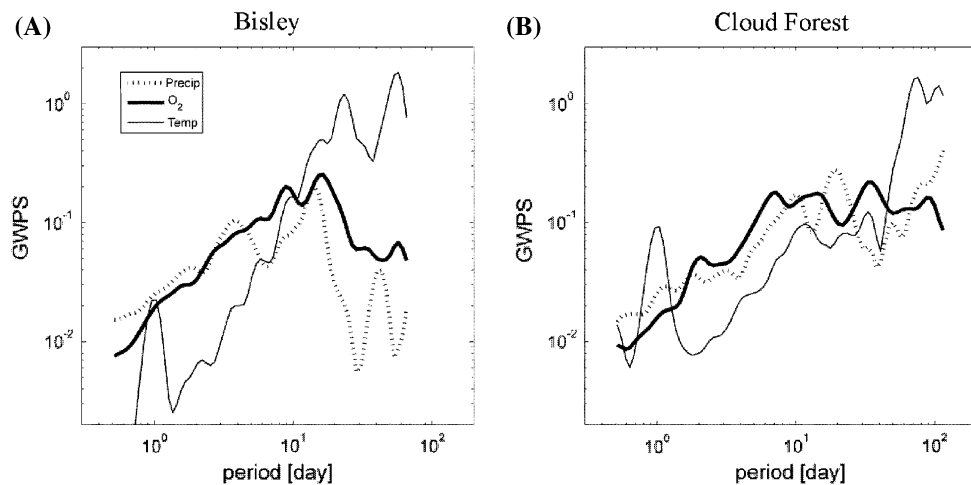

Figure 3. Global wavelet power spectra (GWPS) for hourly chamber O_2, air temperature, and precipitation at Bisley (**A**) and the cloud forest (**B**) sites. The lines represent the power of the spectra at a range of periodicities. Only temperature displays a strong periodicity at daily (10^0) time scales whereas precipitation and O_2 exhibit the greatest power in the spectra at periods of 1–2 weeks.
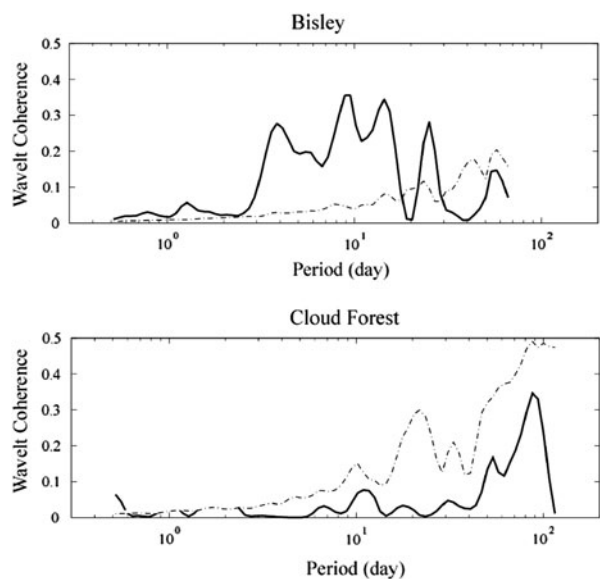
Figure 4. Global wavelet coherence for hourly chamber O_2 and precipitation at Bisley and cloud forest sites. *Dashed lines* represent the 95% confidence interval such that higher values represent significant coherence between the O_2 and precipitation time series.
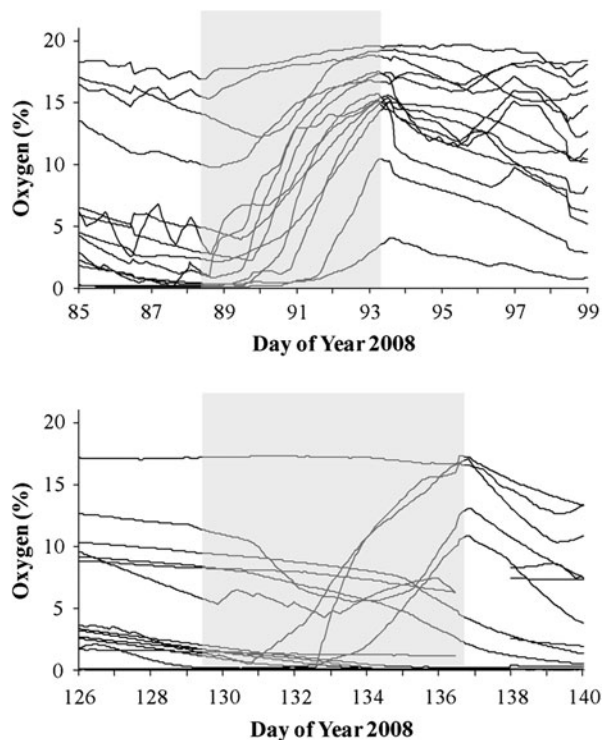

Figure 5. The response of soil oxygen to dry periods in Bisley (**A**) and cloud forest (**B**) with the period of less than 1 mm rainfall per day shaded in *gray*.

The sites differed significantly in trace gas concentrations. Concentrations of N_2O were higher and CO_2 and CH_4 were lower in Bisley than in the

Table 2. Frequency of Dry Periods (Consecutive Days with Less than 1 mm Rainfall) at Bisley and Cloud Forest Sites for 2007 and 2008 Encompassing the Study Period for Both Forest Types

Length of dry period (days)	Bisley		Cloud	
	2007	2008	2007	2008
1	32	36	24	41
2	7	16	8	9
3	9	10	8	5
4	3	4	1	3
5	0	1	0	0
6	0	0	1	1
7	1	0	0	0
8	1	0	0	0
9	1	1	2	0
10	0	0	0	0
11	1	0	0	0
12	1	0	1	0

Table 3. Mean (+1 SE) Chamber Gas Concentrations by Site Calculated from Chamber Averages (n = 14 Bisley, n = 15 Cloud Forest)

	Bisley	Cloud Forest
O_2 overall (%)	7.9 (1.1)	3.0 (0.8)
O_2 sampling (%)	9.3 (1.4)	3.3 (0.8)
CO_2 (%)	6.7 (0.6)	9.2 (1.0)
N_2O (ppm)	23.0 (5.4)	0.3 (0.1)
CH_4 (ppm)	1.7 (0.2)	771.7 (802.7)

O_2 overall is the average of the entire sampling period and O_2 sampling is the mean of the concentrations when the trace gas sampling was done. All of the site differences are significantly different ($P < 0.05$).

cloud forest with almost no overlap of values between sites for N_2O and CH_4 (Table 3). The cumulative probability distributions differed both among trace gases and among sites (Figure 6). The soil CO_2 concentrations were in the percent range at both sites. Although the range of concentrations differed between sites, there was a relatively even distribution at both sites. The shape of the N_2O distribution was also similar between sites. Whereas N_2O was sometimes not detectable in the cloud forest soils, at Bisley the concentrations were always greater than atmospheric concentrations ($\sim$320 ppb). Both the shape and the range of the distribution of CH_4 differed among sites. There was a relatively narrow range of CH_4 concentrations in Bisley, typically near or below atmospheric concentrations ($\sim$1.8 ppm), but reaching as high as 68 ppm. There was a much wider range in CH_4
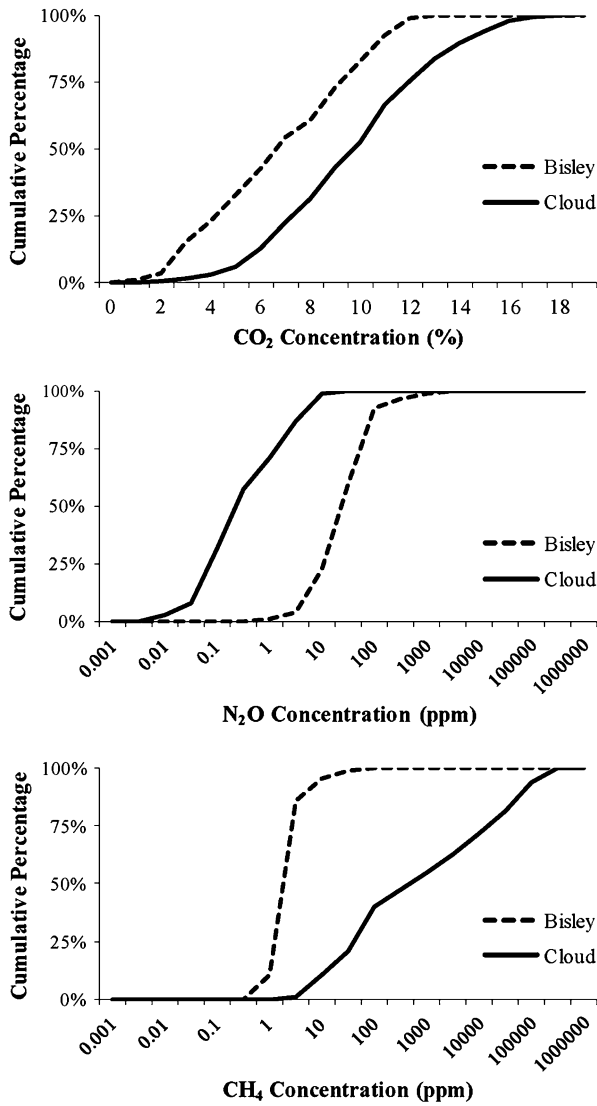
Figure 6. The cumulative percent of all observations of the trace gases CO_2, CH_4, and N_2O.

Table 4. Correlation Coefficients (r) Among all Soil Gases Within Buried Equilibration Chambers with Data Combined from Both Sites

	O_2	CH_4	CO_2	N_2O
O_2	1	-0.60	-0.69	0.62
CH_4	-0.60	1	0.62	-0.85
CO_2	-0.69	0.62	1	-0.57
N_2O	0.62	-0.85	-0.57	1

All correlations are significant at $P < 0.001$.
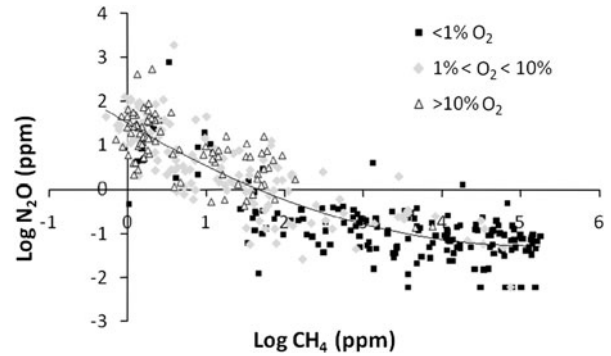
Figure 7. Relationship between N_2O and CH_4 across sites as related to O_2 concentration.
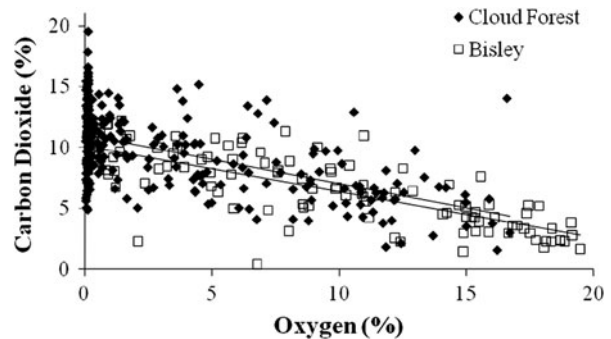

Figure 8. Relationship between CO_2 and O_2 for both sites. Each point represents an individual sample from a buried equilibration chamber. The best fit linear relationship between O_2 and CO_2 is $CO_2 = -0.40 * O_2 + 11.0$, $R^2 = 0.31$, $P < 0.001$ for the cloud forest and $CO_2 = -0.38 * O_2 + 10.2$, $R^2 = 0.60$, $P < 0.001$.

concentrations at the cloud forest site with concentrations spanning from 1.3 ppm up to 17%.

There were significant relationships among the concentrations of the four gases measured. The correlation between O_2 and N_2O was positive as was the correlation between CO_2 and CH_4. Both O_2 and N_2O were negatively correlated with CO_2 and CH_4 (Table 4). Across both the sites, we found a strong negative correlation between N_2O and CH_4, but the concentrations of these gases also depended on O_2 concentrations. When O_2 concentrations were less than 1%, N_2O concentrations were generally at or below atmospheric concentrations and CH_4 was generally above 50 ppm and often above 1% (Figure 7). Although soil CO_2 concentrations were on average higher at the cloud forest site, the

relationship between CO_2 and O_2 was almost identical for the two sites with $CO_2 = -0.38 * O_2 + 10.2$ ($R^2 = 0.6$, $P < 0.0001$) for Bisley and $CO_2 = -0.4 * O_2 + 11.0$ ($R^2 = 0.3$, $P < 0.0001$) for the cloud forest (Figure 8). To highlight the general trends in relationships of the trace gases and O_2, we created 10 equal size bins based on O_2 concentration for the entire trace gas dataset. This approach highlights the strong negative linear relationship with CO_2, as well as the strong negative non-linear
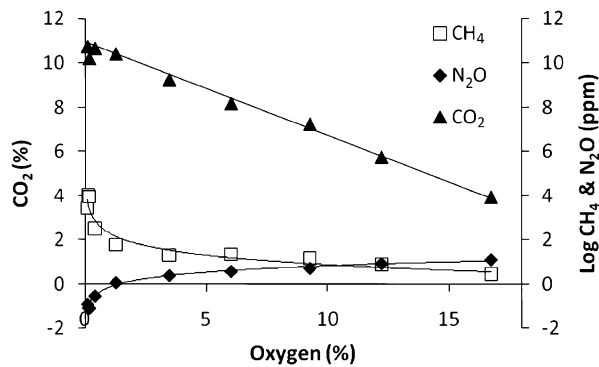
Figure 9. Overall relationship between O_2 and trace gases. The values were divided into ten equal size bins by O_2 concentration and a median trace gas concentration is shown for each bin.
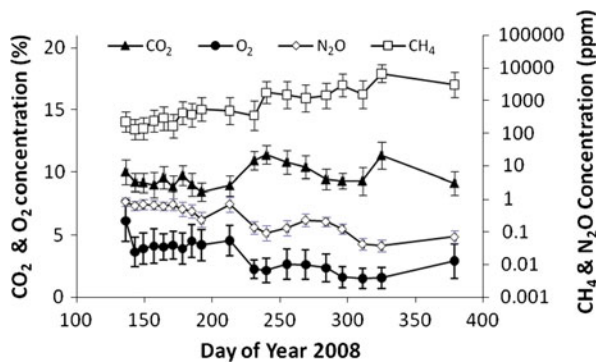

Figure 10. Temporal dynamics of trace gases and oxygen from buried equilibration chambers for the cloud forest site.

and positive nonlinear relationships with CH_4 and N_2O (Figure 9). The overall temporal trends in trace gases were weak, especially compared to the spatial variability. In the cloud forest, there were some general trends over time with O_2 and N_2O decreasing and CH_4 increasing (Figure 10).

DISCUSSION

Soil O_2

The effects of O_2 depletion on the biogeochemistry of flooded soils have been well documented (for example, Gambrell and Patrick 1978; Ponnamperuma 1972), but little is known about the frequency and importance of anoxia in upland soils. Our results suggest that oxic conditions are not the norm for these wet tropical forest soils. In many parts of the cloud forest site, the soils remained anoxic for months at a time, more similar to wetland environments. This is not surprising given that

the ecosystem exhibits characteristics of low O_2 environments like sub-aerial roots (Weaver and others 1986), high soil organic matter content (Silver and others 1999; McGroddy and Silver 2000), and low net primary productivity (Weaver and Murphy 1990). In Bisley, most of the chambers experienced anoxia at some point, but overall the cumulative distribution of O_2 concentrations was relatively uniform. That is, across the whole sampling period and across all sensors there was essentially an equal probability of any O_2 concentration between 0 and 21% (atmospheric O_2). Spatial variability was also high as O_2 concentrations in chambers located just meters apart could be positively or negatively correlated or uncorrelated with each other.

The temporal dynamics in soil O_2 were strongly associated with the frequency, but not necessarily the amount, of precipitation. Soil O_2 concentrations rose during dry periods and fell during rainy periods. These fluctuations in O_2 concentrations were especially prominent during dry periods lasting several days, suggesting strong nonlinear dynamics. Although the number and length of dry periods were greater in Bisley than in the cloud forest, long dry periods (typically 5–8 days) were accompanied by rising O_2 concentration in both sites. Soil O_2 concentrations dropped very rapidly (within a few hours) after even relatively small rainfall events (~ 1 mm), but would only continue dropping if the rainfall continued. During periods with consistent daily rainfall O_2 concentrations still varied, but not in conjunction with the amount of precipitation. The strongest periodicities in the WPS were from 10 to 16 days in Bisley consistent with the observed cycles of dry and wet periods. The frequency of these dry periods varied spatially and temporally in these forests. For example, the total number of days without (< 1 mm) rain was higher in 2008 than 2007 at both sites. However, in 2008 the dry periods tended to be shorter (3 days or fewer in length) with no long dry periods in the cloud forest. In contrast, in 2007, there were several time periods of at least a week with no rain in the cloud forest ($n = 3$) and Bisley ($n = 5$) (F. Scatena, personal communication). If climate change alters the precipitation patterns such that dry periods become more common, an increase in the frequency and magnitude of redox fluctuations would be likely, especially at the cloud forest site. Likewise, if climate change results in wetter climates, the soils could experience more prolonged periods of low O_2 and greater CH_4 concentrations.

Soil O_2 concentrations reflect the net balance of O_2 supply and demand based on physical processes

and biological activity. The rapidity of the response of soil O_2 concentrations to precipitation events suggests that the physical processes, such as the displacement of air by water in soil pore spaces, dominate. However, biological processes could play a role as well. In tropical rain forest soils, C mineralization may be governed by dissolved organic matter leaching from the litter into the soil (Cleveland and Townsend 2006). Thus, without rainfall, C availability and O_2 demand may actually decline. Experiments manipulating water and C availability simultaneously could help separate these two effects.

Plants also affect and are affected by soil redox conditions. At the ecosystem level, the plant community is often less diverse in highly anoxic environments. In Luquillo, the cloud forest canopy is entirely dominated by just five species with just a small fraction of the number of tree species present at lower elevations (Weaver and others 1986; Weaver and Murphy 1990). Special structures, like aerenchymatous tissue, pneumatophores, lenticels, stilt roots help plants survive the various types of low redox environments ranging from high elevation cloud forests to coastal mangrove swamps (Benzing 1991). At smaller spatial scales, plants also actively influence redox-sensitive processes. Plants alter the chemical environment in the rhizosphere affecting the rates of mineral weathering and nutrient cycling (Fimmen and others 2008; Weiss and others 2005). The physical structure of plants can increase the emissions of gases, in particular methane, from anoxic soils, to the atmosphere (Cicerone and Shetter 1981).

Trace Gases

The concentrations of trace gases differed significantly between the two sites, but their relationships with O_2 were similar. The average N_2O concentrations were an order of magnitude higher in Bisley compared to the cloud forest. Nitrous oxide was typically higher than atmospheric levels in Bisley suggesting net production in the soil. At the cellular level, N_2O production and consumption are thought to be controlled by the availability of O_2, nitrate, and organic C (Firestone and Davidson 1989). In soils, N_2O is predicted to be the most common product of nitrification and dentrification at intermediate soil moisture with soil moisture as a proxy for soil O_2 (Davidson and others 2000). In this study, it was somewhat unexpected to see N_2O concentrations increase monotonically with O_2, such that N_2O concentrations were highest at near atmospheric O_2 concentrations. This differs from

the unimodal N_2O–O_2 relationship observed along a soil catena in the adjacent Icacos watershed in Puerto Rico (McSwiney and others 2001). These authors found N_2O concentrations were highest at intermediate O_2 concentrations. If N_2O was produced during denitrification, it would have been occurring in anaerobic microsites in Bisley under the more oxic conditions. Because the soils were often relatively oxic, nitrification could also be an important source of N_2O (Bollmann and Conrad 1998). In the cloud forest, where soil O_2 was consistently very low, denitrification to N_2 was likely to be more important. The measured N_2O concentrations were lower than background atmospheric levels which suggest consumption of atmospheric N_2O.

Methane concentrations were on average more than three orders of magnitude larger in the cloud forest soils than in Bisley, but as with N_2O the relationship between O_2 and CH_4 was similar across sites. In both sites, the relationship between O_2 and CH_4 was strongly nonlinear. High methane concentrations (that is, $>1\%$) were only observed when bulk soil O_2 was less than 1%, but these high concentrations were quite common. The O_2 concentrations were low and relatively static in the cloud forest soils. This persistent anoxia appears to have resulted in considerable methanogenesis. Although the current study only quantified concentrations of CH_4, others have measured net CH_4 efflux from similar sites in Bisley and the cloud forest (Silver and others 1999; Teh and others 2005).

Carbon dioxide concentrations were much less variable between sites than the other greenhouse gases, but like the others, soil O_2 was a strong predictor of CO_2 concentrations. Theory would predict a 1:1 M relationship of CO_2 production and O_2 consumption during organic C mineralization to CO_2 with O_2 as the dominant electron acceptor. This is not always observed in the field, however (Teh and others 2005; Iiyama and Hasegawa 2009), and was not observed here. The relationship could vary from the predicted 1:1 relationship because there are other processes in soils besides aerobic C mineralization that could result in CO_2 production (for example, heterotrophic denitrification, Fe reduction, methanotrophy, acetoclastic methanogenesis) or consumption (hydrogenotrophic methanogenesis) as well as geochemical reactions and root activity that can produce and consume O_2 or CO_2 in the soil. The slope of the observed O_2–CO_2 relationship in this study was much shallower than -1. If CO_2 production from alternative electron acceptors were contributing, the slope would be

steeper. The lack of a 1:1 relationship may be due to the relatively high soil moisture content typical of these soils combined with high biological activity. A significant fraction of the total CO_2 may be dissolved in the soil water instead of in air-filled pores. The Henry's law constant is 27 times higher for CO_2 than O_2 (Gevantman 2010) thus the slope of the O_2–CO_2 relationship should be shallower than -1, but will depend on the proportion of water-filled pore space (WFPS): as WFPS increases, the slope of the relationship becomes increasingly shallow because relatively more CO_2 will be in solution compared to O_2. At the end of the study period, the WFPS calculated following Elliott and others (1999) was 70% in Bisley, based on a gravimetric water content of 73% and a bulk density of 0.7 (Silver and others 1994). Using these values and Henry's law predicts a slope of -0.36, almost identical to the observed regression slope -0.38. Some of the scatter around the regression line may be associated with changes in soil moisture which would change the slope of the relationship even without changes in production or consumption of either gas.

The strong negative relationship between CO_2 and O_2 concentrations in soils does not necessarily translate into higher CO_2 fluxes in low O_2 environments. Surface fluxes are the net balance of consumption, production, and transport of CO_2. High soil CO_2 concentrations may be the result of slow diffusion if most soil pores are filled with water during low O_2 conditions. When other high and low O_2 sites in the same watershed were compared, the high O_2 site had higher surface fluxes (Teh and others 2005). However, when Luquillo soils were incubated in the lab, CO_2 production did not vary significantly between oxic and anoxic treatments suggesting that anoxia per se does not limit C oxidation (DeAngelis and others 2010). These results highlight the fact that O_2 can serve two functions in soils: accepting electrons and activating oxidative extracellular enzymes (Kristensen and others 1995). During anoxic periods, the former can be carried out by other terminal electron acceptors; the latter may be unimportant if the anoxic periods are relatively short in duration. That is, if there is sufficient labile C available during short anoxic periods or fluctuating redox conditions, then the lack of oxidative enzyme activity and associated breakdown of lignin molecules to simpler compounds would not limit overall C oxidation. In contrast, for soils or sediments that remain anoxic for months, the lack of O_2 may result in slow decomposition and higher soil organic C content because there is relatively little breakdown of complex organic matter. In part, the significantly higher soil C in the cloud forest may be due to persistent anoxia. In Bisley, significant C oxidization could consistently occur as soils do periodically experience relatively oxic conditions.

The heterogeneous redox environment in these wet tropical forest soils presents challenges to predicting biogeochemistry, especially in the Bisley site. However, the ability to measure O_2 continuously with sensors provides a major opportunity to improve our understanding of spatial and temporal biogeochemical dynamics. Although the mean O_2 concentration often responded to precipitation events, the periodicity in the O_2 and precipitation records exhibited the strongest coherence during rain-free periods of 5 or more days, allowing the soils time to dry down. The timing, not the amount, of rainfall appears to be a major driver of soil redox environment. Further, although the relationships between O_2 and greenhouse gas concentrations in the soils were highly predictable, they were also strongly nonlinear for N_2O and CH_4. The fluctuating and often reducing soil environment driven by the timing of precipitation appears to be related to high concentrations of greenhouse gases in surface soils.

Redox has long been recognized as a major control on biogeochemical cycling. However, it has only rarely been quantified in upland soils. The results of this study highlight the spatial and temporal scale of variability in soil O_2, and the strong linkages with the timing of precipitation events in these humid environments. The ability to measure O_2 dynamics with continuously logging sensors should vastly improve our understanding of the spatial and temporal patterns of soil redox. These precipitation-driven redox fluctuations may play a crucial role in ecosystem structure and function for several reasons: (1) low and fluctuating redox dynamics appear to drive soil greenhouse gas concentrations in complex but predictable ways, (2) periods of higher and lower O_2 availability may increase microbial diversity as many different metabolic strategies would be favored as redox conditions changed (Pett-Ridge and Firestone 2005; DeAngelis and others 2010), and (3) redox fluctuations may be associated with Fe reduction (Dubinsky and others 2010) and the release of labile P from geochemically associated pools, thus contributing to high NPP in P-poor soils (Chacon and others 2006; Liptzin and Silver 2009). Redox fluctuations are likely to play an important role in a wide range of upland ecosystems that experience perhumid conditions such as wet tropical forests, as well as those characterized by intense precipitation events and periods of soil saturation.

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