Optimal hydrologic regime for regenerating FeIII electron acceptors for iron reduction in upland soils

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Abstract

In the predominantly oxic, upland soils, periods of high wetness trigger anaerobic processes such as iron (Fe) reduction within the soil microsites, with implications for organic matter decomposition, the fate of pollutants, and nutrient cycling. In fluctuating O conditions, Fe reduction is maintained by the re-oxidation of ferrous iron, which renews the electron acceptor, Fe, for microbial Fe reduction. To characterize such processes, it is fundamental to relate the redox cycling of iron between the two redox states to the hydro-climatic conditions. Here, we link iron cycling to soil moisture variability through a model of iron-redox dynamics and find the hydrologic regime that maximizes Fe reduction, under non-limiting organic carbon availability. Away from the optimal cycle, the duration of the oxic or the anoxic phase limits the regeneration of Fe or its reduction rate, respectively. We relate the average duration of the oxic and anoxic intervals to the frequency and mean depth of precipitation events that drive the dynamics of soil moisture, effectively linking iron cycling to the hydrologic regime. We then compare a tropical (Luquillo CZO) and a subtropical (Calhoun CZO) forest to provide insights into the soil moisture control on iron-redox dynamics in these ecosystems. The tropical site maintains a high potential for iron reduction throughout the year, due to quick and frequent transitions between oxic and anoxic conditions, whereas the subtropical site is strongly affected by seasonality, which limits iron reduction to winter and early-spring months with higher precipitation and lower evaporative demand.

O t d e e f e e e t Fe e e t e t s f ed t d s s

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he optimal o ic ano ic c cle or iron e reduction is highlighted
he o ic ano ic c cle and e reduction are related to the soil moisture and rain all variabilit
dro climate control on e reduction potential is studied in a tropical and a sub tropical orest

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n the predominantl o ic, upland soils, periods o high etness trigger anaerobic pro cesses such as iron e reduction ithin the soil microsites, ith implications or organic matter decomposition, the ate o pollutants, and nutrient c cling n uctuating con ditions, e reduction is maintained b the re o idation o errous iron, hich rene s the electron acceptor, e , or microbial e reduction o characteri e such processes, it is undamental to relate the redo c cling o iron bet een the t o redo states to the h dro climatic conditions ere, e lin iron c cling to soil moisture variabilit through a model o iron redo d namics and nd the h drologic regime that ma imi es e reduction, un der non limiting organic carbon availabilit a rom the optimal c cle, the duration o the o ic or the ano ic phase limits the regeneration o e or its reduction rate, re spectivel e relate the average duration o the o ic and ano ic intervals to the re uenc and mean depth o precipitation events that drive the d namics o soil moisture, e ec tivel lin ing iron c cling to the h drologic regime e then compare a tropical u uillo C and a subtropical Calhoun C orest to provide insights into the soil moisture control on iron redo d namics in these ecos stems he tropical site maintains a high potential or iron reduction throughout the ear, due to uic and re uent transitions bet een o ic and ano ic conditions, hereas the subtropical site is strongl a ected b seasonalit , hich limits iron reduction to inter and earl spring months ith higher precipitation and lo er evaporative demand

ron e pla s a critical role in terrestrial ecos stems, in uencing rom the carbon c cle to the mobili ation o contaminants and the ormation o colloidal particles t thus important to understand and uanti its biogeochemical c cle in relation to the envi ronmental actors that drive it, or e ample the o gen content in the soil pores ere, e couple its redo c cle, consisting o e reduction and subse uent e o idation, to the in situ rain all and soil moisture variabilit and sho that the c cle is aster or a spe ci c h dro climate hese results represent an important step to ards predicting the po tential or iron redo c cling across di erent climate and identi the climatic regions here the e biogeochemical c cle ma participate more activel in ecos stem unction ing

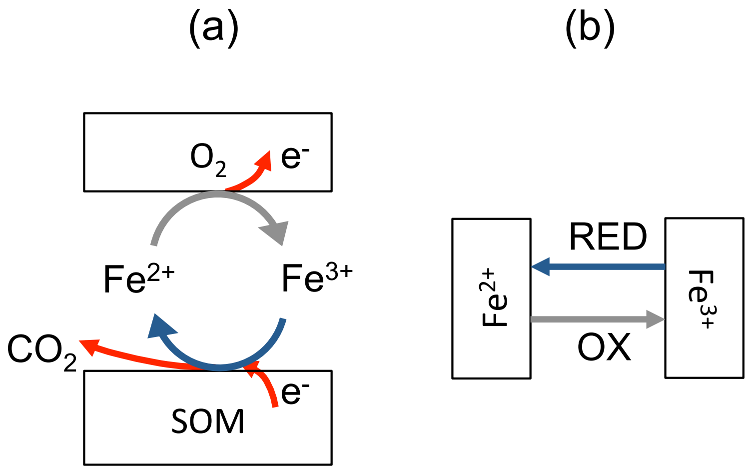
he iron e biogeochemical c cle is an important component o terrestrial ecos s tems, here it is implicated in the decomposition o the organic matter erndon et al , 2017 hattachar a et al , 2018 Calabrese orporato, 2019 ermeire et al , 2019 an et al , 2019 heng et al , 2019 aCroi et al , 2019 , the ormation o colloids Stuc i, 2011 enderson et al , 2012 ang et al , 2019 and mobili ation o contaminants orch et al , 2009 ishop et al , 2014 Couture et al , 2015 u et al , 2016 redicting the vari ations in e reduction rates as a unction o the h dro climatic re uires lin ing processes rom the pedon to the atershed scale, but this has been challenging because o the nu merous actors that a ect the e redo chemistr

he undamental constraint on the e redo d namics is the reduction o e , hich has slo er inetics than the o idation o e ovle , 1991 inn et al , 2017 Chen hompson, 2017 uring ano ic conditions, e reducing microorganisms rel on the availabilit o e o ides as an electron acceptor, reducing it to errous iron e in order to decompose the organic matter ovle , 1991 oden et el, 1996 ubins et al , 2010 he rate o e reduction thus depends on a suitable organic substrate a o e an Cappellen, 2011 , the activit o e reducers, as ell as the abundance o e electron acceptor relative to other more thermod namicall avorable ones e g , , n he energ ield obtained rom o idi ing organic matter coupled to e as electron acceptor is lo er than the energ ield obtained hen coupled to hus, e reduc tion is strongl dependent upon the availabilit o an easil degradable substrate a o e an Cappellen, 2011 , hereas those substrates that re uire more energ to o idi e i e , have higher values or the C o idation hal reaction can become thermod namicall un avorable or microbial e reduction he abundance and activit e reducers is critical or predicting e reduction rates aborator and eld observations both have sho n that e reduction is aster hen the soil has e perienced e reduction in the re cent past uettner et al , 2014 arcellos, C le, hompson, 2018 , suggesting increased e reducers activit in these conditions astl , higher reduction rates are driven mostl b recentl o idi ed e eiss et al , 2004, 2005 hompson et al , 2006 he avail abilit o e electron acceptor can in act be uanti ed through measurements o short range ordered e minerals

he above arguments suggest that e reduction rates are strongl controlled b the characteristics o the soil o ic ano ic c cles n act, in ell aerated soils o ic conditions , iron mostl remains in its o idi ed state e and aerobic respiration is the main mech anism o carbon decomposition, hereas in nearl constantl ano ic environments, such as etlands or padd soils, iron ma persist in its reduced state e and other metabolisms t pical o lo redo potentials ma be triggered, i e , ermentation or methanogenesis orel et al , 1993 rad eil, 2016 et een these e treme scenarios, a continu ous transitions bet een o ic and ano ic conditions e g , et tropical soils, river ban s, uctuating ater tables , hich spurs the ormation o degradable organic substrates, higher activit o e reducers, and the continuous regeneration o e , ma avor high rates o iron reduction Calabrese orporato, 2019

he main environmental actor controlling the transitions bet een o ic and ano ic conditions is the soil ater content odd ro n et al , 2012 rad eil, 2016 , as this determines the activit o aerobic bacteria and the raction o air lled volume perimental studies sho that soil moisture ma be a pro or o gen content, because this remains relativel high 20 or ater contents up to the soil eld capacit and then nonlinearl declines to 0 as the soil approaches saturation all et al , 2013 arcellos, Connell, et al , 2018 uanti cation o the ate and redo changes o soil iron, necessar or the understanding o the global carbon c cle and related climate d namics Colombo et al , 2014 ertel et al , 2016 heng et al , 2019 , then needs to be carried out in relation to ho h dro climatic variabilit can induce changes in soil aer ation and redo potential

o ards this goal, e derive the relationship bet een the average e reduction rate and the length o e posure to o ic and ano ic conditions, hich is related to the h dro logic regime means o a mechanistic iron redo model, e e plore the interaction bet een the timescales o the biogeochemistr i e , the reaction rates and o the changes in environmental conditions i e , o ic ano ic c cle and highlight the e istence o a ma imum average e reduction rate at an intermediate ano ic o ic intervals ratio e then relate the o ic ano ic c cle to the h dro climatic uctuations and lin the characteris tics o the c cle to the statistical properties o the soil moisture d namics and precip itation, in terms o its re uenc and mean rain all depth his e ectivel lin s iron re duction to the in situ h dro climatic variabilit , or hich measurements are readil ob tained through direct or remote sensing techni ues ppl ing the rame or to soils rom a humid tropical orest u uillo C and a subtropical orest Calhoun C , e e plore the iron redo d namics in these di erent ecos stems and discuss its control on the carbon c cle and plant primar productivit

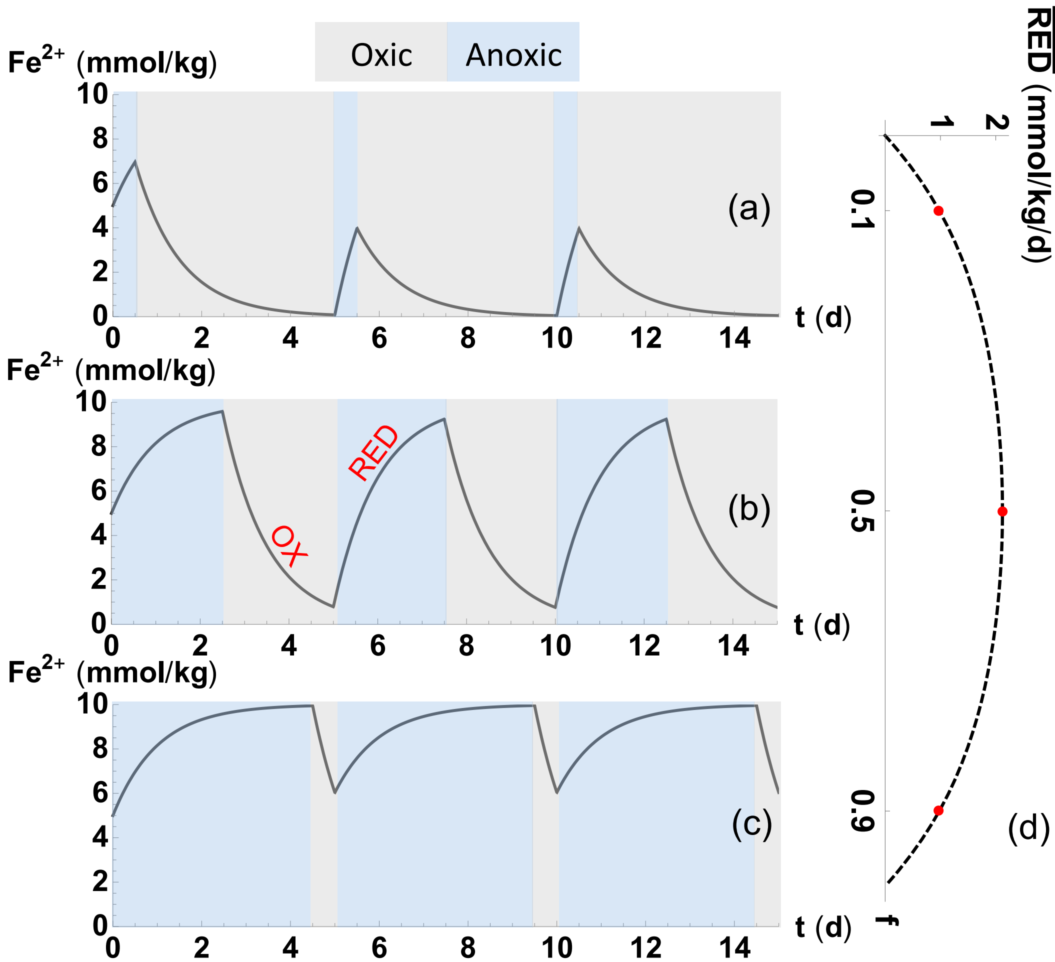


he soil iron c cle, summari ed in igure 1 a , has an ano ic phase, in hich e is utili ed as an electron acceptor to decompose organic matter and an o ic phase, hen o gen o idi es e , thus regenerating the e pool oing bac and orth bet een the t o o idation states, iron operates as an electron carrier bet een the soil organic matter and the atmospheric o gen igure 1 a , so that the decomposition depends on the rate at hich electrons can be transported rom the organic matter to o gen e composition b iron reduction in act needs a continuous suppl o iron e, hich after having been reduced to e during a ano ic phase needs to be regenerated i e , re o idi ed during the subse uent o ic phase t is thus clear that the h dro climate generating the o ic ano ic c cles e erts a ma or control on the rate o iron c cling

Consider the top soil la er containing organic matter and re er to the total iron content in the o idi ed and reduced states as F and F , respectivel he total content o reducible iron is constant and e ual to F F F Since our ocus is on the ma imum rates, e assume that the availabilit o the organic substrate and microbes does not limit the reactions, so that the regeneration o e electron acceptor and presence absence o ano ic conditions limit the reaction he h drologic c cle ill thus govern the reaction rates in this rame or he soil is sub ect to an o ic ano ic c cle o duration T that begins ith the ano ic phase o duration fT igure 2 , hereas the o ic phase lasts or 1 f T, f being the ano ic raction uring the ano ic phase, onl iron reduction occurs no o idation allo ed , ith a conse uent increase o F uring the o ic phase, iron reduction stops and F is o idi ed to F igure 1 b Such d namics are described b the ollo ing mass balance e uation,

$$\frac{dF}{dt} \quad R \qquad (1)$$

here R k F F and k F , k and k being the reduction and o idation rate constants, respectivel ote that these e pressions do not contain a dependence on the amount o substrate and microbial activit , as e are ocusing e clusivel on the h drologic regime o ever, the rate constants do e plicitl depend on the time, t, in that during the ano ic phase k 0, hile during the o ic phase k



f

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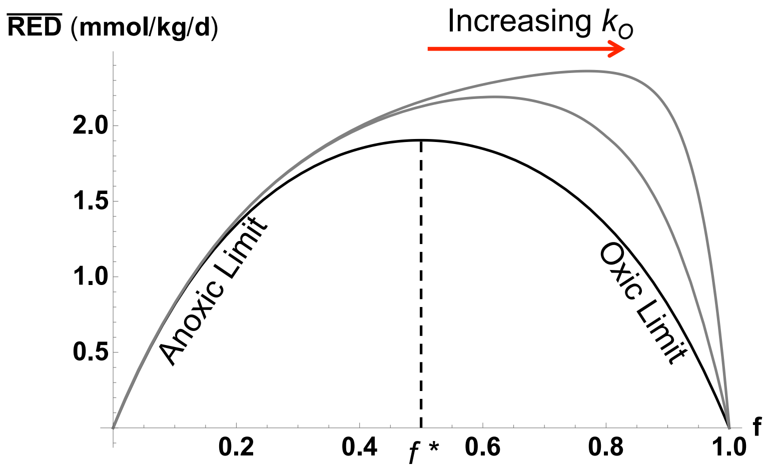

R
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0 Solving e uation 1 or su cientl long time such that the initial condition has no longer in uence, the stationar solution or a given o ic ano ic c cle sho n in igure 2 a is given b an e ponential deca during the o ic phase,

$$F \quad t \quad F \quad e^{\;o} \tag{2}$$

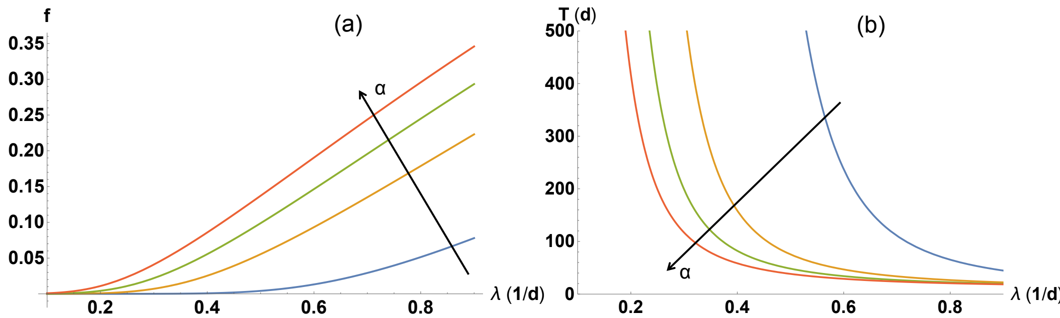
here F is the iron content at the end o the preceding ano ic phase and t is the time elapsed since the beginning o the o ic phase n the contrar , during the ano ic phase F increases, approaching e ponentiall F ,

$$F \quad t \quad F \qquad F^{\,0} e^{\;o} \tag{3}$$

$F^{\,0}$ being the iron content at the end o the preceding o ic phase and t the time elapsed since the beginning o the ano ic phase

n an e treme scenario, in hich conditions are set to be al a s o ic f 0, ig ure 2 , iron content persists in its o idi ed state F t 0, and the average reduc tion rate, hich can be de ned as $\overline{R}$ 1 T R $t\, t$, goes to ero n the other hand, or a scenario o constant ano ic conditions f 1, igure 2 iron persists in its reduced state, F t F , and again the reduction rate $\overline{R}$ 0 his argu ment suggests that a ma imum reduction rate $\overline{R}$ e ists at an intermediate value o f, f Solving e uation 1 or di erent values of f, the di erent e tra ectories are sho n in igure 2, and computing the average reduction rate per c cle, see igure 2 d , illus trates the ano ic o ic c cle or hich the $\overline{R}$ is ma imum

he optimal f at hich the ma imum e is achieved depends on the reaction rate constants, k and k or simplicit , igure 2 demonstrates that, in the h pothet ical condition in hich k k , the resulting f 0 .5 or higher k or k , shorter ano ic or o ic phases are needed to reduce or o idi e the same amount o iron, respec tivel s the ratio o ano ic o ic time moves a a rom the optimal f, the o ic ano ic c cles is avoring either the reduction f f or the o idation f f , leading to an inhibition o e c cling hen f f , the iron redo c cle is limited b the regen eration o e electron acceptor, as essentiall there is not enough time to o idi e enough su cient iron to use in the ollo ing ano ic phase n the contrar , hen f f the iron redo c cle is limited b the e reduction, such that the ano ic phase is too short to reduce substantial amounts o iron igure 3



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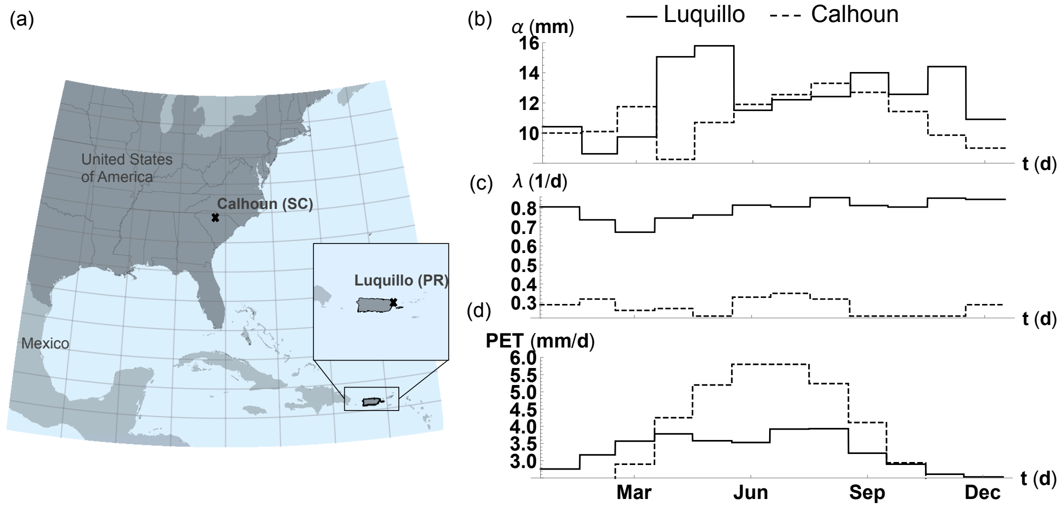
PET k

nder eld conditions, the re uenc and depth o the rain all events, evapo transpiration rom soil and plants, and soil properties altogether determine the evolution o the soil ater and o gen content, causing the soil to undergo transitions bet een o ic and ano ic conditions Since o gen content e hibits a rst dependence on soil moisture all et al , 2013 Calabrese orporato, 2019 , the average duration o the o ic and ano ic phases, or a given h dro climate, can be obtained b anal ing the speci c time series o soil moisture i ing the soil moisture threshold s above hich soil conditions can be con sidered ano ic there are enough ano ic soil microsites to activate anaerobic processes , the average time spent in o ic conditions then can be calculated as the average time o each e cursion belo the threshold s he average time o each e cursion above s ill be , the average duration o a o ic ano ic c cle T , and in turn the ano ic raction o time f /

e sho the relationship bet een the ano ic raction f, c cle length T and the re uenc and mean depth o precipitation λ and α, respectivel in igure 4 he curves are dra n or constant soil properties t pical o a silt cla loam and potential evap otranspiration PET 4 mm d using a stochastic ater balance that provides the statistical properties o soil moisture based on rain all statistics aio et al , 2001 see ppendi ecause o the high ater losses at soil moisture above eld capacit , the raction o time spent in ano ic conditions is generall lo er than the one spent in o ic conditions, such that the values o f are belo 0.5 igure 4 s can be e pected, soils are in ano ic conditions on average longer higher values o f or high rain all re uen cies accompanied b high average rain all depths n the contrar , the hole duration o the c cle, T, decreases ith λ as the e cursion rom o ic to ano ic is more li el to occur or the realistic range o mean rain all depth α and re uenc λ e plored, the length o the ull ano ic and o ic c cle T decreases ith α, again because it becomes more li el that the soil moisture threshold s is crossed o ever, or ver high mean rain all depth α and re uenc λ the trend in igure 4 ma be inverted as the soil s itches to ver et conditions that are in ano ic conditions s s or most o the time



he comprehensive h drological and biogeochemical observations at the tropical orest in u uillo uerto ico and at the subtropical orest in Calhoun South Car olina , hich are part o the Critical one research net or sponsored b the S a tional Science oundation, allo us to readil appl the above rame or to compare the soil iron d namics and the potential or iron reduction in these di erent environments n u uillo, e ocus on the isle atershed, here man e c cling studies have been per ormed t that site, the mean annual precipitation is about 3 5 m and the vegeta tion belongs to the abonuco orest t pe Scatena, 1989 Soils are predominantl l tisols, ormed rom volcanic parent material, and belong to the silt cla loam te tural class Calhoun has mean annual precipitation o appro imatel 1250 mm and vegeta tion includes mi ed hard ood and pine trees ere soils are also predominantl ltisols, ormed rom a granite gneiss bedroc , and belong to the silt loam te tural class ichter ar e it , 2001

onthl averaged mean depth and re uenc o precipitation as ell as potential evapotranspiration or the t o sites are illustrated in igure 5 hile u uillo has a hu mid tropical climate ith onl a mild seasonalit slightl reduced rain all in the in ter season , Calhoun has a subtropical climate ith mar ed seasonalit in both precip itation and evaporative demand, une and ul being the ettest months ith also a pea in potential evapotranspiration eochemical anal sis sho ed that u uillo and Calhoun soils have appro imatel 150 and 45 mmol, respectivel , o short range ordered or lo cr stallinit e phases per ilogram o soil inn et al , 2017 arcellos, C le, homp son, 2018 arcellos, 2018 Soil incubation e periments ith soil samples rom both sites amended ith substrate and microbes revealed that reduction rate constants are o the

Figure 6. (a) Temporal evolution of soil moisture, simulated by means of the stochastic model in (Laio et al., 2001), in Luquillo (blue line) and Calhoun (green line) over the course of a year. Soils are silty clay loams and silty loams in Luquillo and Calhoun, respectively, with porosity of 0.48. Soil hydrologic properties for the simulation of the soil moisture dynamics from Fernandez-Illescas et al. (2001). Soils are considered to have sufficient anoxic microsites to support Fe reduction for soil moisture levels above $\hat{s} = 0.85$ in Luquillo and $\hat{s} = 0.75$ in Calhoun. (b) Anoxic fraction of the cycle, f, and (c) duration of the cycle, T, for each month computed by means of equations (??) and (??) in the Appendix. (d) Temporal evolution of Fe^{II} in Luquillo (gray line) and Calhoun (red line) over the course of a year, simulated through equation (1). The reduction and oxidation rate constants are $k_R = 0.1$ and $k_O = 10$ mmol/kg/d, respectively.

order of 10^{-1} d^{-1}, while the oxidation rate constants at 21% O_2 are of the order of 10 d^{-1} (Chen & Thompson, 2017; Ginn et al., 2017).

4.2 Oxic/anoxic cycles and iron reduction

To calculate the temporal dynamics of potential iron reduction (when limited only by the hydrologic regime), we solved equation (1) coupled to a soil water balance that generates a time series of soil moisture levels based on the frequency and mean depth of precipitation events (Figure 6). For Luquillo these rainfall statistics are available in Heartsill-Scalley et al. (2007) and Calabrese and Porporato (2019), while in Calhoun they were obtained combining multiple sources ("http://criticalzone.org/calhoun/data/datasets/" and "https://www.usclimatedata.com/climate/south-carolina/united-states/3210"). The average anoxic fraction f and cycle length T of the oxic/anoxic cycles are then computed for each month from the probability density function of soil moisture (see Appendix A). Note that for each month the parameters f and T are computed assuming stationary climatic conditions. For each month their values thus correspond to oxic/anoxic cycles that would occur if the climatic conditions were stationary and typical of that specific month. As a consequence, it can happen that the value of T is greater than the duration of the month, e.g., T = 80 days in Calhoun in September. Of course, these large values of T for a particular month only indicate that it is very unlikely to observe full redox cycles (an Fe oxidation event and an Fe reduction event) in that given month, typically because soil moisture remains below the threshold set.

In Luquillo, the soil moisture frequently crosses the $\hat{s}$ threshold, generating redox cycles of only a few days (2-3 days) throughout the year (Figure 6(a) and (c)). Similarly, the calculated anoxic fraction f remains practically constant during the year and approximately equal to 0.3 (Figure 6(b)). The mild seasonality here is almost not visible in the

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