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# A new synthesis for terrestrial nitrogen inputs

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## Abstract

Nitrogen (N) inputs sustain many different aspects of local soil processes, their services, and their interactions with the broader Earth system. We present a new synthesis for terrestrial N inputs that considers both rock and atmospheric sources. We review evidence for state-factor regulation over biological N fixation, deposition and rock weathering inputs from local to global scales and in transient vs. steady-state landscapes. Our framework highlights strong organism and topographic (relief) controls over all three N input pathways, with the anthropogenic factor clearly important in rising N deposition rates. In addition, the climate, parent material and time factors are shown to influence patterns of fixation and rock-weathering inputs of N in diverse soil-systems. Data reanalysis suggests that weathering of N-rich parent material could resolve several known cases of “missing N inputs” in ecosystems, and demonstrates how the inclusion of rock N sources into modern concepts can lead to a richer understanding of spatial and temporal patterns of ecosystem N availability. For example, explicit consideration of rock N inputs into classic pedogenic models (e.g., Walker and Syers model) yields a fundamentally different expectation from the standard case: weathering of N-rich parent material could enhance N availability and facilitate terrestrial succession in developmentally young sites even in the absence of N-fixing organisms. We conclude that a state-factor framework for N complements our growing understanding multiple-source controls on phosphorus and cation availability in Earth’s soil; but with significant exceptions given the lack of an N fixation analogue in all other biogeochemical cycles. Rather, a state-factor analysis of N must recognize non-symmetrical feedbacks among input pathways, whereby high N inputs via deposition or rock weathering have the potential to reduce biological fixation rates within a given state-factor.

## 1 Introduction

Nutrients have a long-standing and demonstrated importance in the pattern and regulation of soil-systems, their services, and their functioning across Earth's diverse environments. An extensive literature has been developed around the concept that biologically essential elements, particularly nitrogen (N) and phosphorus (P), influence patterns of plant productivity, biodiversity and soil carbon (C) contents from temperate to tropical biomes (Jenny, 1980; Vitousek, 1984; Vitousek and Howarth, 1991; McGroddy et al., 2004; Elser et al., 2007; Cleveland et al., 2013; Fernández-Martínez et al., 2014). Classical soil paradigms have focused on primary nutrient input paths to ecosystems – via rocks vs. atmospheric sources – and how such inputs vary as a function of soil-forming state factors – time, parent material, biota, climate, and topographic relief (Jenny, 1941). New nutrient inputs are necessary for the maintenance of soil fertility, rejuvenating persistent ecosystem losses to erosion, leaching and the atmosphere (Schlesinger and Bernhardt, 2013). The demonstrative importance of nutrient input principles is therefore embedded in seminal work by Walker and Syers, Jenny, and Vitousek and colleagues, making a substantial contribution to environmental soil science, ecology, biogeochemistry and global change.

Traditional concepts have argued for age-related declines in nutrient inputs via rock weathering sources over the long-term course of pedogenesis. While fresh parent material is often high in P and cations, Walker and Syers (1976) suggested that weathering and erosion deplete these elements in primary substrates, with progressive P occlusion into biologically unavailable pools over millions of years of ecosystem development. Work by Jenny et al. (1969) in the Mendocino terraces has led to the concept of the terminal steady-state in stable landforms in which rock weathering inputs cease and profound P-depletion results in severe stunting of forest vegetation over millennia (Izquierdo et al., 2013). Vitousek and Farrington (1997) used direct fertilization experiments to show that P becomes progressively limiting to terrestrial productivity in old Hawaiian sites, following long-term declines in soil P availability in highly weathered volcanic soils (Crews et al., 1995). These patterns of retrogression – the systemic decline in soil fertility and productivity over primary succession – have been observed widely in chronosequence studies across latitudes, lending support to the idea that soils and ecosystems progress interminably toward a state of profound nutrient depletion (Wardle et al., 2004; Vitousek et al., 2010).

More recently, several workers have shown that the atmosphere can play a vital role in cation and P nutrition, with landscape scale features altering the trajectory of soil development compared to flat stable surfaces in highly weathered landscapes. Work in highly weathered tropical sites demonstrates the importance of long-distance dust transport in sustaining soil P and cation fertility (Chadwick et al., 1999). A recent union of the more traditional pedogenic models with landscape principles shows that erosion can re-set the clock of ecosystem development, such that rock-derived elements can once again play a substantial role in otherwise highly weathered and P-limited ecosystems (Vitousek et al., 2003; Porder et al., 2005; Porder et al., 2006). Newer models have thereby been devised to explicitly address controls of tectonic uplift, erosion, climate, time and atmospheric transport on patterns of P, silicon (Si) and cation inputs to soil (Okin et al., 2004; Vitousek, 2004; Hilley and Porder, 2008; Mahowald et al., 2008; Hartmann et al., 2014). This growing appreciation for atmospheric and rock sources has substantially enriched our understanding of variations in soil fertility and nutrient limitation predictions in complex environmental landscapes (Vitousek, 2004).

In contrast, a complementary (and multi-input) framework is lacking for N, despite the widespread control of this nutrient over many aspects of global ecosystem services and functioning (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008). Rather, this nutrient is widely considered to be derived solely from the atmosphere (Delwiche, 1970; Vitousek et al., 1997; Galloway et al., 2004; Ciais, 2013; Fowler et al., 2013). Textbook paradigms emphasize biological N fixation (the conversion of $N_2$ to bio-available N forms) and atmospheric N deposition inputs to local ecosystem (Bormann and Likens, 1979; Vitousek, 2004) and global N balances (Schlesinger, 1997), neglecting potential contributions from N weathering reactions (but see Schlesinger and Bernhardt, 2013;

Vitousek et al., 2013). Controls on fixation and deposition have been examined and discussed extensively (Vitousek et al., 2002; Galloway et al., 2004; Lamarque et al., 2005; Reed et al., 2011), and models have accounted for these N inputs in climate change and global carbon storage projections (Thornton et al., 2007; Wang and Houlton, 2009; Zaehle et al., 2010b; Ciais, 2013).

Nevertheless, a growing body of evidence suggests that geological N inputs to the soil have been overlooked. Just like P, cations and trace metals are weathered into soil from parent material pools, so is fixed N, the largest reservoir of which exists in crustal rocks (Schlesinger, 1997). Thus, it's not surprising that rock N sources have been shown to affect patterns of soil fertility (Strathouse et al., 1980), ecosystem functioning (Dahlgren, 1994; Holloway et al., 1998), and terrestrial C storage across an array of ecosystems (Morford et al., 2011). Although the global implication of rock N inputs remains uncertain, geochemical models have pointed to the importance of N weathering in regulating atmospheric $N_2$ over deep time (Berner, 2006), and past reviews suggest that rock N sources are widespread throughout the land surface (Holloway and Dahlgren, 2002). We suggest that a new synthesis of atmospheric and rock N inputs is vital to advancing our understanding of the functioning of soils and ecosystems across the diversity of Earth's environments.

Here, we present a state-factor framework for atmospheric vs. rock N sources to help guide future research into N input patterns and magnitudes in diverse soil-systems. Our objective is to present a general approach to N fixation, deposition and rock N inputs within the context of known ecosystem state factor controls, using case studies, consilience and analogy to advance our understanding of soil N cycling broadly. We also make reference to elements other than N (i.e., P, cations) – particularly in the case of rock N inputs – to infer likely patterns of N inputs where research is less well-developed. Additionally, we discuss implications of a new paradigm for terrestrial N inputs, such as those related to terrestrial C storage, soil fertility, climate change and widespread changes to N cycling via human actions.

## 2 Ecosystem state-factors

We devise a state-factor framework for terrestrial N inputs into soils and ecosystems. We emphasize regulation, pattern and interaction of N inputs with soil pattern and process, across local, landscape and global scales. Our approach takes advantage of Jenny's system (1941), which has been applied widely to other nutrients (e.g., Vitousek, 2004), wherein five ecosystem state-factors are used to understand soil fertility and pedogenic patterns across the Earth system. The five factors include parent material, climate, organisms, topography (or relief) and time (Jenny, 1941). In addition, given the importance of human actions on Earth's biogeochemistry, we include an anthropogenic factor in our analysis here, consistent with previous calls for this sixth factor (Amundson and Jenny, 1991).

Our review is not necessarily deep into any given N input path: for in-depth reviews on N fixation see Vitousek et al. (2002) and Reed et al. (2011); N deposition see Lovett (1994) and Lamarque et al. (2005); and rock N chemistry see Holloway and Dahlgren (2002). Rather, our aim is to examine how different state factors broadly influence the distribution and magnitude of atmospheric vs. rock N sources, with case studies presented throughout our synthesis.

### 2.1 Climate

Climate is among the chief regulators of terrestrial N input paths and magnitudes, particularly N fixation and rock weathering sources across soil-systems. Biological N fixation is mediated by nitrogenase, an enzyme which exhibits a steep temperature-dependency and high activation energy (Cueterick et al., 1978). A global compilation of data has revealed that the effect of temperature on N fixation is apparent across a range of organisms, latitudes and soil conditions, in which nitrogenase activity approaches a global optimum at $\sim 25$ degrees centigrade (Fig. 1). Knowledge of the T-sensitivity of fixation across global ecosystems has been used to model rates of N fixation in the soil (Houlton et al., 2008; Wang and Houlton, 2009), resolving patterns of N fixation that are otherwise paradoxical (Jenny, 1950; Crews, 1999). For example, symbiotic N fixing trees are absent from many high latitude sites, despite the preponderance of evidence for substantial N limitation in many temperate and boreal forests (Crews 1999). In contrast, putative fixers in the Fabaceae family (i.e., legumes) are abundant in lowland tropical forests and savanna ecosystems where several metrics point to an abundance of N (Martinelli et al., 1999; Hedin et al., 2009). Consideration of the climate-factor helps explain this pattern: temperature limits rates of fixation at higher latitudes where energy/C is limiting, effectively increasing the C cost of fixation beyond its manifold benefits for organism functioning (Houlton et al., 2008). Global models suggest that climate warming could thus stimulate fixation at high latitudes, whereas low-latitude tropical sites may exhibit declines in this important N input pathway (Wang and Houlton, 2009; Ciais, 2013).

Rock weathering is also sensitive to temperature; but the water balance of the ecosystem (i.e., precipitation – evapotranspiration) appears central to chemical weathering rates across landscapes (Kump et al., 2000; Chadwick et al., 2003). Excess moisture increases the volume of water moving through soil and rock pores and accelerates mineral dissolution. While temperature is a primary factor in kinetic models of mineral dissolution (Lasaga et al., 1994), direct temperature effects may be attenuated by pore water residence time (i.e. fluid flow) in most soils in practice (Maher, 2010). Indirectly, temperature alters ecosystem water balances by influencing evapotranspiration, water phase and biological activity, but these effects have been difficult to disentangle in the field (Amundson et al., 2007).

Field derived weathering rates generally increase across climatic-gradients. Catchment scale silica fluxes (White and Blum, 1995) and soil clay content (Jenny, 1941) are positively correlated with increasing temperature plus precipitation. Further, investigations of soil climosequences show that soil development and weathering rates are maximized in warm and wet sites (Dahlgren et al., 1997; Egli et al., 2003; Rasmussen et al., 2007; Williams et al., 2010). However, the temperature-sensitivity of weathering has been difficult to isolate in field settings, and appears to vary as a function soil water-balance (Rasmussen et al., 2011) and/or biological factors (Riebe et al., 2004). Particularly for biologically important elements (P, nutrient cations), the temperature sensitivity of field-derived weathering rates may be substantially lower than laboratory-derived activation energy estimates. This could explain why observations for soil P weathering rates are commonly more sensitive to precipitation than temperature (Smeck, 1973; Birkeland et al., 1989; Porder and Chadwick, 2009). Rates of rock N weathering are similarly affected by climate; high N weathering rates are seen in warm/moist environments, with the ecosystem water balance a particularly dominant control over N weathering inputs to plant-soil systems (Morford, 2014).

## 2.2 Organisms

We suggest that the organism factor plays both a direct and indirect role in the pattern and regulation of all three terrestrial N input pathways. This factor is self-evident and direct in the case of N fixation; the presence of organisms with the capacity to fix N is requisite to this input path, though legacy effects that play out in slowly cycling soil N pools can obscure the link between fixer populations and N input-output balances in modern ecosystems (e.g., Perakis et al., 2011). Globally, organisms with the capacity to fix N symbiotically are much more abundant in tropical than temperate forests (Crews, 1999; Menge et al., 2014), with evidence for increased rates of N fixation following disturbance (i.e., forest gaps) in many ecosystems (Binkley et al., 1994; Rastetter et al., 2001; Vitousek et al., 2002; Davidson et al., 2007; Davidson, 2008; Barron et al., 2011; Batterman et al., 2013). Likewise, rates of symbiotic N fixation are generally higher in tropical than temperate forests (Cleveland et al., 1999; Houlton et al., 2008) – following global patterns in legume abundance (Crews, 1999) – and in disturbed sites at higher latitudes – particularly where various populations of *Alnus* sp. (alder) and *Ceanothus* sp. dominate in post-fire sites where energy (light) is abundant (Vitousek and Field, 1999; Smithwick et al., 2005). Further, studies of N-fixing gene abundance (*nifH*) in the soil have demonstrated a high degree of correlation between free-living microbial fixers and N fixation rates in ecosystems (Reed et al., 2011).

Binkley et al. (1994) found that populations of *Alnus* sp. symbiotically fixes anywhere from 50 to 100 kg N ha$^{-1}$ yr$^{-1}$ in mixed stands and up to 200 kg N ha$^{-1}$ yr$^{-1}$ in mono-dominant ones, with relatively persistent rates where this species was present in Pacific Northwest sites. Studies in the Adirondack Mountains in New York found evidence for high rates N fixation ($\sim$ 47 kg N ha$^{-1}$ yr$^{-1}$) by this species in recently disturbed and riparian zone sites (Hurd et al., 2001), though workers in Wisconsin reported low rates of N fixation ($<$ 5 kg N ha$^{-1}$ yr$^{-1}$) by *Alnus* sp. across a range of stand conditions (Younger and Kapustka, 1983). Where *Ceanothus* sp. is present in early to mid-successional forest sites, typically following fire, this species has been shown to fix anywhere from 4 to $>$ 100 kg N/hr/yr (Smithwick et al., 2005).

Jenny (1950) suggested that unexpectedly high soil N pools in many lowland tropical sites reflected the presence of symbiotic N fixers within this biome, an idea that has been confirmed by some (Batterman et al., 2013) though not all studies in lowland tropical forests (Vitousek et al., 2002; Barron et al., 2011; Sullivan et al., 2014b). Indeed, legume populations vary markedly within the Amazon basin (from 10 % to $\sim$ 50 % of stems/plot, ter Steege et al., 2006), with model-based fluxes suggesting anywhere from zero to $>$ 100 kg N ha$^{-1}$ fixed via symbiotic pathways within this expansive ecosystem (Wang and Houlton, 2009). Moreover, Vitousek et al. (1987) demonstrated a strong link between the organism factor and N inputs in their study of *Myrica faya*, an invasive fixer that increased N inputs by $\sim$ 5 times and soil inorganic N pools by $>$ 3 times in N-limited native Hawaiian rainforest.

The general consensus from these studies is that the presence of fixers points to N fixation input capacity, though nodulation is a species-dependent property that varies across ecosystem conditions (Sylvester-Bradley et al., 1980; Sprent and Raven, 1985); hence it's paramount to verify and not assume N fixation inputs in the field. Further, spatial coherence between fixers' abundance patterns and high rates of soil N accumulation is not always apparent owing to a host of localized controls and temporal dynamics in the N fixation process (Walker et al., 1993; Vitousek et al., 2002; Reed et al., 2011). For example, Perakis et al. (2011) demonstrated that high N fixation rates by *Alnus* sp.

in early succession resulted in high soil N cycling and availability in non-fixing Douglas fir stands for decades. This kind of temporal dynamism, in which fixers are long-since absent from sites where fixation inputs were high, continues to challenge our ability to address relationships between terrestrial N fixation, soil N fertility, and ecosystem N losses (Hedin et al., 2009; Perakis et al., 2011; Sullivan et al., 2014b).

In addition to direct effects, an important indirect role of the organism factor is also apparent in atmospheric N inputs – particularly via dry deposition and cloudwater N – for which community composition and forest structure act to modify local N deposition inputs to soil (Lovett, 1994). Conifers generally show higher N throughfall fluxes than broadleaf vegetation, reflecting greater surface area and surface roughness that facilitates higher rates of dry-deposition scavenging from the air (Lovett, 1994). For example, an extensive study in Europe reported N throughfall fluxes under conifer canopies that exceeded bulk N deposition rates by a factor of ~4 (i.e., 41 vs. 12 kg N $ha^{-1}$ $yr^{-1}$, Kristensen et al., 2004). Another major influence of the organism-factor on local N deposition inputs is seen in comparisons of forest gaps and canopy edges. Lindberg and Owens (1992) reported much higher nitrate throughfall fluxes in mature spruce forest edges than in localized gaps and forest interiors. They attributed this difference to localized controls on dry N deposition rates, which are affected by forest structure, aspect and exposure in highly fragmented ecosystems.

Beyond the atmosphere, geobiological controls in the organism factor are widely known to influence the physical and chemical weathering of rock-derived elements generally. This occurs though direct and indirect mechanisms. For example, “rock-eating-fungi” have been shown to directly accelerate the weathering of calcium ($Ca^{2+}$)- and potassium ($K^+$)-bearing lithologies in forests (Jongmans et al., 1997; van Scholl et al., 2008). Past work points to mycorrhizal fungi (i.e., root symbionts) in the weathering of feldspar minerals via the production of various organic acids and chelates – succinate, citrate, oxalate, formate and malate – that chemically deplete rock minerals actively (Jongmans et al., 1997; Hoffland et al., 2004; van Scholl et al., 2006; van Scholl et al., 2008). Other mechanisms include the production of siderophores, particularly via ecotomycorrhizae (ECM), which bind iron and thereby accelerate soil mineral weathering and horizon development (Taylor et al., 2009). Indirectly, plant investment in belowground root and hyphal networks enhance reactive mineral surfaces and provide C for microbial decomposition. The resulting increase in soil $CO_2$ and chemical reaction sites could enhance chemical weathering rates by a factor of 2–10 (Drever, 1994; Andrews and Schlesinger, 2001). Such vegetation-driven weathering rates in upland ecosystems have been suggested to vary with atmospheric $CO_2$ concentrations over the past 24 million years (Pagani et al., 2009).

Although less is known about direct geobiological controls on soil N weathering reactions, isotopic evidence suggests that N can be directly transferred from rocks to plants in ecosystems, which might be mediated by fungal mutualism (Fig. 2). The isotopic composition ($\delta^{15}N$) of rock N sources (green line) can be exceedingly enriched compared to atmospheric N inputs (Holloway and Dahlgren, 2002; Houlton and Bai, 2009), which are typically between 0 to −3 per mil (dashed line). Across a set of temperate forest sites dominated by Douglas fir, the $\delta^{15}N$ of foliage converges on that of rock $\delta^{15}N$ when rock concentrations exceed ∼ 500 ppm N; yet soil $\delta^{15}N$ is consistently higher than rocks and other N input pathways as the result of fractionating losses of N (Martinelli et al., 1999; Amundson et al., 2003; Houlton et al., 2006; Houlton and Bai, 2009). This suggests active uptake of rock N by plants in N-rich parent material, which is likely to be facilitated by root-associated ECM in Douglas fir forests. Examining this hypothesis in a range of sites by measuring mycorrhizal abundance, N concentrations and $\delta^{15}N$ of various N pools is deserving of future work.

## 2.3 Topography

Topographic relief alters rates of erosion and chemical weathering; this factor affects N fixation (discussed in Parent Material below) and could strongly affect rock N inputs to soil. Global biogeochemical analysis points to widespread control of tectonics, uplift and orogeny on the removal of elements from the land (Stallard and Edmond, 1983; Raymo et al., 1988; Milliman and Syvitski, 1992; Stallard, 1998). Under the steady-state, relief is seen as the balance between uplift and erosion, with active orogens representing potential “hot-spots” of rock-derived element availability in the soil. At landscape scales, denudation (combined physical erosion plus chemical weathering) increases with local relief exponentially (Montgomery and Brandon, 2002; Portenga and Bierman, 2011). Both empirical data (Stallard and Edmond, 1983; Riebe et al., 2004; West et al., 2005) and theoretical models (Gabet and Mudd, 2009) show that chemical weathering is maximized in landscapes with moderate to high erosion owing to the rapid exhumation of fresh reactive minerals. At very high erosion rates, however, chemical-weathering rates may decline due to thinning of the regolith and soils, effectively reducing the amount of reactive surface area available for chemical weathering.

Among landscapes with high relief, soil nutrient availability reflects a dynamic tension between chemical weathering and erosion. Work by Porder et al. (2007) suggested that rock-derived nutrient availability ought to peak at moderate uplift rates where there the ratio of weathering inputs/losses reaches achieves a global maximum. Among stable landforms, low denudation rates greatly reduce element inputs via rocks; in contrast, high relief environments often display high chemical weathering rates but large element losses to erosion and mass wasting – thereby limiting the accumulation of soil available nutrients. Model-based abstractions of these geomorphic principles suggest that lowland tropical sites in stable landforms are likely to be P-limited, whereas areas of moderate relief and high chemical weathering are less likely to be limited by P (Porder et al., 2007; Porder and Hilley, 2011).

Within landscapes, topographic relief controls how rocks and soils are distributed along hillslope positions. Both weathering rates and erosion in hillslope sequences are generally highest among shoulder and backslope positions, contributing to accumulation of weathering products in low relief footslopes and toeslopes (Milne, 1936; Gessler et al., 2000; Yoo et al., 2007). Consequently, the highest rates of weathering become spatially decoupled from where nutrient accumulation (and putatively plant nutrient availability) is greatest (Yoo et al., 2006, 2007). Weathering rates at summit positions are variable, but among stable summit positions weathering rates are generally lowest. These conditions can promote long-term declines in soil fertility and functioning over millennia, perhaps best demonstrated in highly weathered stable-surfaces where the stunted Pygmy forest occurs in Mendocino, California (Jenny et al., 1969; Izquierdo et al., 2013). Landslides can remove soil that is highly weathered and provide biological access to un-weathered parent material; this mechanism has been demonstrated to rejuvenate elements such as P in otherwise P-limited volcanic soils in Hawaii (Vitousek et al., 2003; Porder et al., 2005).

Could similar mechanisms affect rock N inputs in complex landscape settings? The standard hillslope/catena model suggests that N storage and availability should increase downslope: erosion is generally highest among upslope positions, resulting in transport of soluble and particulate N to depositional-footslope positions, a pattern observed for several grassland catena sites (Aandahl, 1948; Schimel et al., 1985). A number of sites developing on N-rich lithologies have exhibited more complex or even opposite trends, however – pointing to potential rock N inputs to soil-landscapes.

For example, upslope (high elevation) sites exhibited substantially higher net N mineralization and nitrification rates, larger soil inorganic N pools, and elevated foliar $^{15}N/^{14}N$ compared to low elevation sites developing on sedimentary (and putatively N-rich, Holloway et al., 1998; Holloway and Dahlgren, 2002) parent material in the Great Smokey Mountains (Garten and Vanmiegroet, 1994). Likewise, total soil N concentrations were elevated in shoulder positions of cantenas underlain by N-rich shale substrates in the Shinga prefecture, Japan (Hirobe et al., 1998). More directly, (Morford et al., 2011) demonstrated that the N content of soils and forest foliage collected from erosional slopes of N-rich metasedimentary rocks (350–950 ppm) was elevated by more than 50 % compared with similar temperate forest sites underlain by N-poor igneous parent material (30–70 ppm). For N-bearing lithologies, this means that rock N inputs could offset local N losses from erosional hillslope positions while also contributing to higher total N inputs at landscape scales – thus altering topography-driven patterns of N availability that are closer to expectations for other rock-derived elements (Morford, 2014).

### 2.4 Parent material

We suggest that the parent material factor regulates patterns and rates of N fixation and rock input pathways. Rocks contain ~ 99 % of Earth's fixed N (Schlesinger, 1997) – recording the legacy of higher rates of N fixation compared to denitrification to $N_2$ gas over Earth history. Nitrogen concentrations are much higher in sedimentary/meta-sedimentary than igneous parent materials, though either class can contain appreciable geological N (Holloway and Dahlgren, 2002). Further, reservoirs of geological N can occur as silicate-bound $NH_4^+$, organic-N in sedimentary organic matter, or nitrate in evaporites. Variation in both the amount and form of rock N is controlled by local depositional environments, the degree of biological and thermal digenesis in sedimentary basis, and the degree of N volatilization during metamorphism (Bebout and Fogel, 1992; Hedges and Keil, 1995; Hedges et al., 1999; Boudou et al., 2008). Rock-bound nitrate can be seen in desert/arid ecosystems where hydrological losses are minimal and nitrate accumulates at depth or in the surface of caliche deposits (Walvoord et al., 2003). On average, Holloway and Dahlgren (2002) found that the parent material factor is a strong driver of rock N contents, with trace amounts of N found in cratonic assemblages to > 20 000 ppm N in sedimentary rocks such as coal.

Several studies have reported a link between the parent material factor and soil N pools in the field. Strathouse et al. (1980) reported substantial quantities of nitrate in relatively young vs. older sediments in the San Joaquin valley, USA; they attributed this difference to the weathering and loss of N from parent material to soil pools over time. Their analysis showed that 15 to 88 % of N was lost from rock minerals over the long time-course of weathering, with sites on N-rich parent substrates showing higher soil N concentrations than those underlain by N-poor sediments. Dahlgren (1994) demonstrated that weathering of mica-schist minerals caused substantial changes in pools of nitrate and ammonium in northern California soils. Morford et al. (2011) used isotopic techniques to directly trace N-rich rocks into soils and vegetation at the same site, demonstrating a doubling in soil and plant N concentrations compared to sites underlain by N-poor diorite. Finally, Dixon et al. (2012) reported high rock N concentrations across a sequence of sites in Sweden; they attributed variations in soil N to variations in N parent material chemistry.

Such N inputs via weathering can both positively and negatively affect terrestrial ecosystem functioning. Weathering of N rich mica-schist was shown to acidify soils in un-vegetated sites in northern California; rapid N release from rock minerals stimulated soil nitrification rates and the production of $H^+$, which in turn elevated labile Al concentrations in mountain-top barrens (Dahlgren, 1994). In contrast, the nearby vegetated sites stored ~ 50 % more C and N in soils compared to N-poor dioritic sites, N weathering inputs more than doubling terrestrial N balances compared to atmospheric N inputs alone (Morford et al., 2011). The substantial effect of N-rich rocks on terrestrial C storage was apparent in forest biomass across the Pacific Northwest region (Morford et al., 2011), suggesting largely beneficial effects of bedrock N on soil fertility and $CO_2$ uptake overall.

The parent material factor also controls atmospheric N inputs. In particularly, biological N fixation responds to changes in trace metals (Mo) and P, owing to the bio-chemical demands of nitrogenase, high ATP requirements, capacity for fixation to adjust rapidly to changes in the availability of P compared to non-fixers, or all three mechanisms (Fig. 3). Both P and Mo have important rock sources, and experiments conducted in a variety of ecosystems support the view that P and Mo can substantially limit fixation in both symbiotic and free-living pathways (Vitousek and Hobbie, 2000; Vitousek et al., 2002; Barron et al., 2009; Reed et al., 2011). Therefore, it is not surprising that research from tropical sites show that rock P chemistry controls the rates and responses of N fixation; sites across volcanic to sedimentary lithologies influenced soil P availability and thus the response of free-living fixation to P vs. Mo (Wurzburger et al., 2012).

### 2.5 Time

Here we emphasize the time factor over primary succession where new ecosystems develop on fresh geologic substrates. Jenny (1958) was perhaps the first to explicitly conceptualize a link between patterns of N fixation and soil N accumulation during primary succession (Fig. 4). He argued that N can be profoundly limiting to plant productivity during the earliest stages of pedogenisis – especially in sites where other N inputs are low – a condition that confers advantage to organisms with the capacity to fix N. Over time, as soil N stocks build sufficiently, non-fixing species can acquire N from the soil at a lower C cost compared to fixation, build extensive canopies, and outcompete fixing species for light and other resources. Hence, the trend of decreasing abundance of biological N fixation is posited as the outcome of physical, chemical and biological controls that alter the competitive balance between fixers and non-fixers during pedogenesis, including effects of herbivory, requirement for other elements especially P and Mo, light competition, evolutionary history and biophysical factors (Vitousek and Field, 1999; Rastetter et al., 2001; Vitousek et al., 2002; Wang et al., 2007; Houlton et al., 2008; Menge et al., 2009; Reed et al., 2011)

Evidence from a variety of ecosystems generally supports the expectation for a decrease in N fixation over primary succession (Walker, 1993). In both newly formed volcanic (Vitousek, 2004) and de-glaciated sediments (Chapin et al., 1994) cyanolichens are among the earliest colonizers, with evidence for significant rates of N fixation in fresh parent material (Crews et al., 2001). These pioneering species provide N to facilitate more diverse ecosystem communities as succession proceeds, but are ultimately excluded owing to light limitations and life-history factors as forest canopies develop further (Chapin et al., 1994; Chapin et al., 2002; Vitousek et al., 2002; Walker et al., 2003). Work along recently deglaciated environments shows that populations of symbiotic fixers have an advantage in early primary succession. Once N pools reach a critical threshold, however, competition favors non-fixing species such as black spruce, which can acquire N from the soil at minimal cost compared to fixation and can outcompete alder for light (Chapin et al., 1994). A similar pattern was found in different New Zealand sites, wherein early colonizing plants with the capacity to fix N were replaced by non-fixing species over the course of primary succession (Walker et al., 2003).

This pattern is not always observed, however – particularly as spatial heterogenetity alters local nutrient availability and decouples of free-living fixers from average soil conditions (Reed et al., 2011). For example, Menge and Hedin (2009) showed that symbiotic N fixation via *Coriaria arborea* averages $\sim 11\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ until $> 60$ years of pedogensis. Thereafter, this species was competitively excluded from older sites along the Franz Josef chonosequence in New Zealand owing to a host of life-history and ecosystem constraints. In contrast, free-living N fixation in various soil pools and the canopy were variable yet persistent during primary succession, consistent with studies of free-living paths along the Hawaii chronosequence (Matzek and Vitousek, 2003). And, work on free-living fixation in the boreal suggests a pattern that opposes Jenny's (1958) model: rates of N fixation in feather moss communities have been shown to increase over primary succession, likely in response to declines in N availability over time (Zackrisson et al., 2004).

Thus, a key implication of past research is that average soil nutrient conditions do not necessarily impose control over non-symbiotic fixation during ecosystem development, and factors constraining symbiotic vs. free-living rates can and do differ from one another (Vitousek et al., 2002; Reed et al., 2011). Free-living fixers experience different environmental conditions in decomposing organic matter, bryophyte mats and as epiphytes in the canopy, and competition for light and dispersal limitations may be less of a factor than observed for symbiotic fixation during succession. More diffusely, however, Benner et al. (2007) showed that application of P fertilizers to a Hawaiian oxisol caused cyano-lichen blooms in the canopy, thus pointing to indirect connections between soil nutrient pools, nutrient limitation, and free-living fixation rates in forests.

In contrast to fixation, knowledge of rock N inputs during primary succession has been comparatively sparse. Most studies assume that rock N inputs are uniformly unimportant in newly formed ecosystems (sensu Walker and Syers, 1976), rather than measuring and examining the potential for rock weathering to alter N inputs over succession. This assumption is probably true for igneous substrates where parent material N contents are typically low (e.g., Hawaii chronosequence, Vitousek, 2004); but not for many sedimentary and meta-sedimentary substrates (see also Parent Material above).

Binkley et al. (2000) analyzed evidence for surprisingly high rates of N accumulation in terrestrial ecosystems as based on knowledge of atmospheric N input pathways. Their assessment placed high confidence in the unexplainably high N accumulation (soil plus vegetation) rates observed for forests in Walker Branch, Tennessee ($> 43$ to $70\,\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$, Johnson and Todd, 1998) where the lithology is dominated by differential sequences of marine carbonate and siliciclastic sediments. In fact, a closer inspection of N accretion studies (Binkley et al., 2000; Johnson and Turner, 2014) reveals that eight of the ten temperate sites with unusually high N accumulation rates (i.e., $> 20\,\mathrm{kg\,ha\,yr^{-1}}$) were from sites with high geologic N input capacities (see Supplement Table S1; Fig. 5). The remaining two sites were from the Hubbard Brook Sandbox experiment (Bormann et al., 1993) and the Mt. Shasta mudflow chronosequence (Dickson and Crocker, 1953) where rock N inputs are unlikely. While a number of the sedimentary sites also showed low (or negative) N accretion rates, there does not appear to be divergent pattern between putatively N-rich vs. N-poor geologic-substrates; yet, nearly all the sites reporting high N accumulation rates come from sites on sedimentary parent materials (Fig. 5). Thus, this reanalysis provides testable evidence that rock N inputs could help explain the “missing N inputs” in a range of temperate forest sites.

## 2.6 Anthropogenic

Humans have become the single-greatest force in terrestrial N inputs, more than doubling the circulation of reactive N in the terrestrial biosphere and shaping N inputs in both natural and managed sites profoundly (Delwiche, 1970; Vitousek et al., 1997; Galloway and Cowling, 2002; Fowler et al., 2013). The anthropogenic factor plays a major role in atmospheric N deposition inputs into natural soil systems; rock mining activities have mobilized geological N but not in a way that has greatly changed N inputs to natural sites. Further, human alternations can be classified as intentional or unintentional (Houlton et al., 2013), with the former arising via fertilizer inputs and domestication of legumes, and the latter as fixed N derived from fossil fuel combustion and air-borne agricultural losses of N.

Hence, the anthropogenic factor has most clearly altered patterns of N deposition inputs into natural or unmanaged soil systems (Holland et al., 1997; Lamarque et al., 2005; Galloway et al., 2008). These airborne sources of N have greatly changed patterns of N deposition inputs from the pre-industrial state, and so N deposition maps well with areas of fertilizer use and industrialization (Fig. 6) – with many unwanted ecosystem consequences (Vitousek et al., 1997). Current estimates suggest that ~30 % of anthropogenic N deposition is derived from fertilizers, with the majority (i.e., 70 %) derived from mobile and stationary fossil fuel sources (Schlesinger, 2009). Whereas the largest post-industrial growth in anthropogenic N deposition has occurred at higher latitudes (Galloway et al., 2004), N deposition inputs to soils and ecosystems are expected to expand to tropical and sub-tropical environments as developing economies grow this century (Matson et al., 1999; Lamarque et al., 2005), as is already clear throughout much of China (Liu et al., 2013).

## 3 Discussion and implications

We propose a state-factor framework for atmospheric and rock N input pathways to complement our understanding of controls on P and cation availability in soil. We view this synthesis as a point of departure; we provide a broad list of controls over what are the most substantial state-factor effects on terrestrial N input patterns and magnitudes, with explicit corollaries for each factor summarized in Table 1. Understanding how state-factors regulate N inputs – including rock and atmospheric sources – to diverse soil-systems is important for three principal reasons.

First, N limitation to terrestrial plant productivity is widespread (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008). Whether N limitation is transient or sustained is largely determined by the magnitude of N inputs, their spatial variation, and balance with respect to N losses from the biosphere (Hedin et al., 1995; Vitousek et al., 2002; Houlton et al., 2003; Houlton and Bai, 2009; Cleveland et al., 2013). A new synthesis that considers both rock and atmospheric N sources, and how such sources are regulated by state-variables, will improve our understanding of N limitation to plant productivity and soil microbial processes across Earth's diverse terrestrial ecosystems. For example, application of state-factor principles has lead to a richer understanding of patterns of P limitation patterns even in the absence of direct empirical experiments (Porder and Hilley, 2011). Fertilization experiments are laborious and difficult to implement in many natural ecosystems (Sullivan et al., 2014a); knowledge of how state-factors are likely to shape the sources of N that dominate different soil environments will improve our understanding of N limitation patterns and processes.

Second, a state-factor framework for N inputs can inform global climate forecasts and terrestrial interactions with N availability. Global biogeochemical projections that consider N availability point to much less $CO_2$ capture and soil C sequestration than C-only models (Hungate et al., 2003; Thornton et al., 2007; Wang and Houlton, 2009; Zaehle et al., 2010a). The recent IPCC AR5 report included only one N cycle model that, when coupled to two different Earth System Models (ESMs), suggested less $CO_2$ uptake and more climate warming than model-runs without an active N component (Ciais, 2013). Moreover, the uncertainty in terrestrial N input paths and C by N interactions could result in up to 2 degrees Celsius of additional warming by 2100 (Wang and Houlton, 2009). However, none of these models have considered N inputs via rock sources, and the potential for this N input path to alter patterns of ecosystem N and C storage (e.g., Morford et al., 2011). Our synthesis points out important controls over rock N inputs by all but one (anthropogenic) state factor, and articulates controls that can be used to inform models that consider all three N input pathways together. All

N input paths can display climate-dependencies, for example, but most clearly in the case of rock N weathering and biological N fixation inputs.

Third, conceptual models that include combinations of factors are necessary to advance our understanding of variation in soil N fertility, such as interactions between time, steady-state and transient landscape dynamics, and parent material chemistry (Fig. 7). Classical pedogenic models have assumed that fixation and deposition can alter patterns of ecosystem development but have hitherto neglected rock N sources (Walker and Syers, 1976). By separating the parent material factor between N-poor vs. N-rich substrates, we propose different trajectories for ecosystem N availability as a function of parent material, organisms, time and topographic relief. Factors that allow for high rock N inputs – N-rich sedimentary rocks, early succession, moderate relief – would be expected to deviate from the standard model of N limitation, whereas N-poor lithologies would be expected to follow previously articulated patterns of nutrient limitation during ecosystem pedogenesis and landform development – with N fixers playing a more active role in early succession (Fig. 7). We recommend experiments that superimpose state factors in natural site arrays (e.g., as done in Hawaii sensu Vitousek, 2004) to systematically isolate controls on N weathering inputs and examine its role in primary succession and landscape patterns of N fertility.

Although we have largely examined state factor controls separately, N input pathways can and do affect one another within a given state-factor setting. For example, theory and experimental research demonstrates that external N inputs reduce the capacity for terrestrial N fixation (Vitousek et al., 2002; Reed et al., 2011; Fig. 3). This occurs generally as the competitive balance shifts in favor of N uptake from the soil, which can occur at a minimal cost compared to N fixation under increasing N concentrations (Vitousek and Field 1999; Rastetter et al., 2001; Houlton et al., 2008). This means that state-factors favoring high N inputs via deposition and rock weathering are likely to affect patterns of N fixation – but less clearly in the converse – potentially reducing rates of fixation in a given soil system. In addition, we expect low N / P parent materials to favor fixation, all else remaining equal.

In fact, the capacity for biological N fixation to respond rapidly to changes in other N input pathways is what marks this element as fundamentally different from all other major soil nutrients. Phosphorus, cations and essential trace metals exhibit both rock and atmospheric input paths that are clearly controlled by state factors; yet they lack important gaseous phases and an N fixation analogue to promote rapid feedback among atmospheric and rock sources. We conclude that ecosystem analysis of N inputs must consider how factors altering the pattern and magnitude of N weathering and deposition can influence fixation, in contrast to state-factor controls on other soil elements in which input-sources are not tied to one another.

Finally, as humanity's imprint on the Earth system expands and intensifies, understanding the global consequences of reactive N inputs to natural soil systems will become increasingly important to soil and ecosystems services. On the one hand, the N saturation hypothesis argues for declines in plant productivity and terrestrial C storage as chronic increases in anthropogenic N deposition inputs acidify soils, cause nutrient imbalances, and mobilize soil $Al^{3+}$ forms to toxic thresholds (Aber et al., 1989). Alternatively, the progressive N limitation hypothesis recognizes the role of rising levels of $CO_2$ in stimulating plant photosynthesis and productivity, and instead argues for enhanced N limitation and growth of soil and ecosystem N sinks (Luo et al., 2004). Both of these hypotheses could play out – with different mechanisms dominating different sites or with progressive N limitations giving way to N saturation effects in individual ecosystems over time. In any case, a greater appreciation for state-factor regulation of the complexity, pattern and magnitude of atmospheric vs. rock N input pathways will go a long way toward understanding how Earth's diverse soils, landscapes and ecosystems will respond to and feedback on unprecedented rates of global environmental change.

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**Table 1.** Generalized state-factor regulation over terrestrial nitrogen (N) inputs.

| State Factor | Biological $N_2$ Fixation | N Deposition | N Chemical Weathering |
|---|---|---|---|
| Climate | Generally increase with temperature; global optimum ~ 25 degrees Celsius | – | Increase with precipitation and to lesser degree with temperature |
| Organism | Presence of fixers increases rate | Local effect; higher in conifers than deciduous vegetation | Increase with productivity and presence of fungal mutualism, geobiological control |
| Parent Material | Higher in P and micronutrient rich substrates | – | Higher in N-rich sedimentary than N-poor igneous substrates |
| Relief | Highest at intermediate relief | Higher at high elevation sites | Highest at intermediate relief |
| Time | Typically high early primary/secondary succession; but can be substantial in highly weathered lowland tropical soils | – | High in early primary succession in N-rich parent material, decreasing importance with weathering and erosion over time |
| Anthropogenic | – | Increase with fossil fuel combustion and synthetic N fertilizer sources | – |

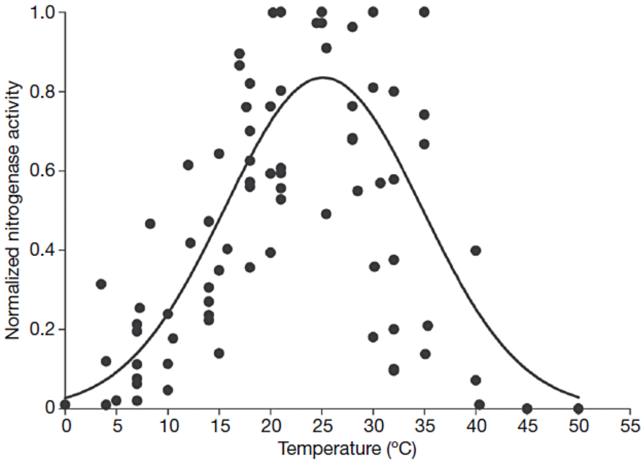

**Figure 1.** Temperature-dependence of terrestrial nitrogenase activity. Data are normalized to the maximal activity observed for each study, which span temperate to tropical latitudes, and different strains and species of N fixing organisms. (From Houlton et al., 2008).

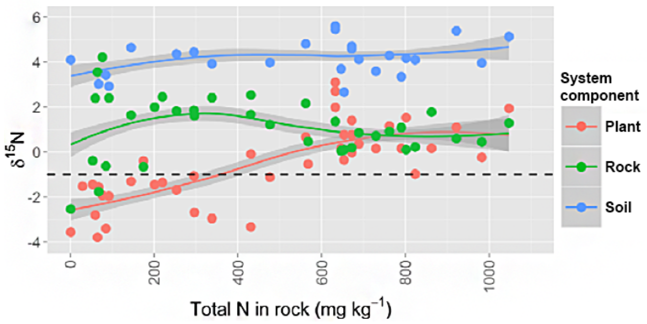

**Figure 2.** $\delta^{15}$N of live foliage, soil and parent material (rock) vs. rock N concentrations across Douglas fir forest. The dashed line reflects that $\delta^{15}$N of atmospheric N inputs. (Morford and Houlton, unpublished).

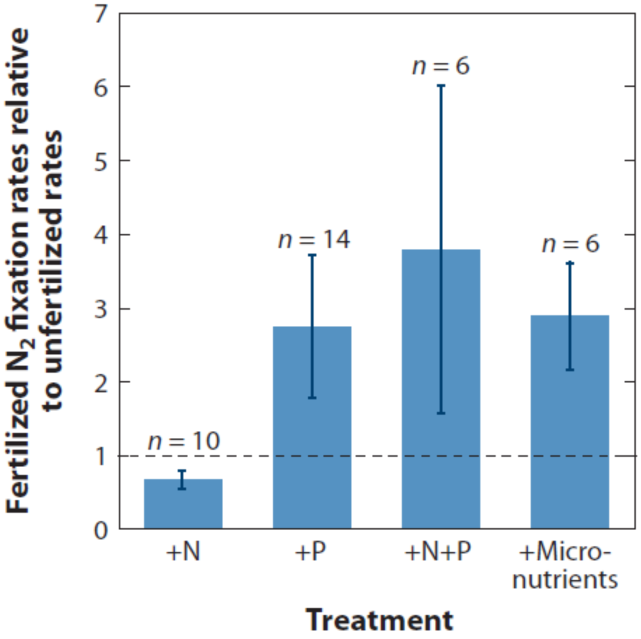

**Figure 3.** Response of free-living N fixation rates to different nutrient fertilization treatments. Values above one on the *y* axis indicate positive response, below indicates a negative response to fertilization by + N, + P, +N +P or + micro-nutrients. (From Reed et al., 2011).

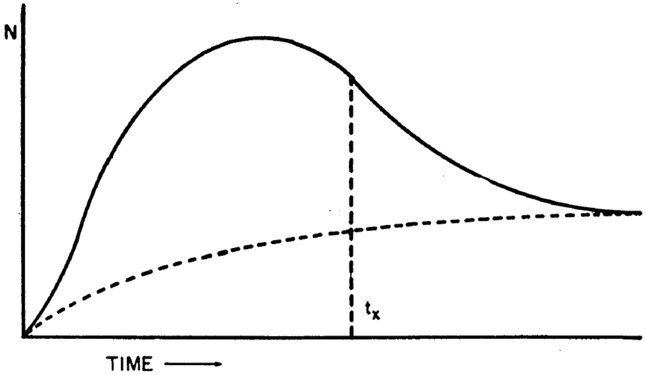

**Figure 4.** Expectations for rates of N accumulation with and without N fixers during primary succession. The solid line depicts high rates of N fixation (i.e., presence of legumes); the dashed line is depicts cases where fixers are absent from early successional sites. (From Jenny, 1958).

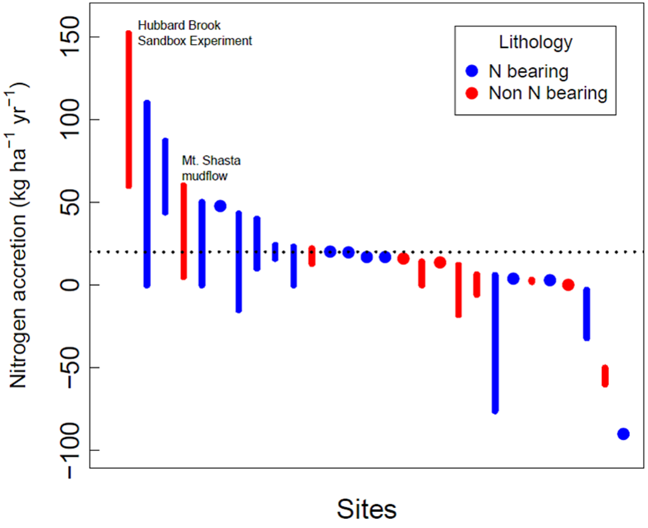

**Figure 5.** Nitrogen accumulation rates in terrestrial ecosystems underlain by N-bearing vs. non N-bearing lithologies. The dashed line is the cut-off for rates of N accumulation that exceed estimates of atmospheric N inputs (i.e., 20 kg N ha$^{-1}$ yr$^{-1}$). See supplemental table for meta-data and N-lithology determination. (Modified reanalysis of Binkley et al., 2000 and Johnson and Turner, 2014).

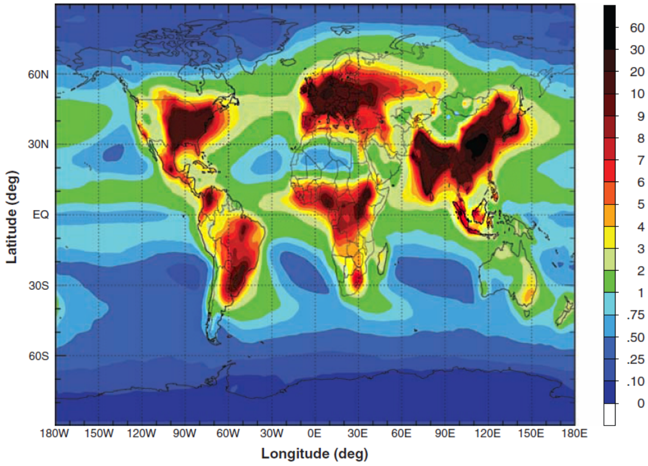

**Figure 6.** Rates of inorganic N deposition rates based on total N emissions in units of kg N ha$^{-1}$ yr$^{-1}$. (modified by Galloway et al., 2008).

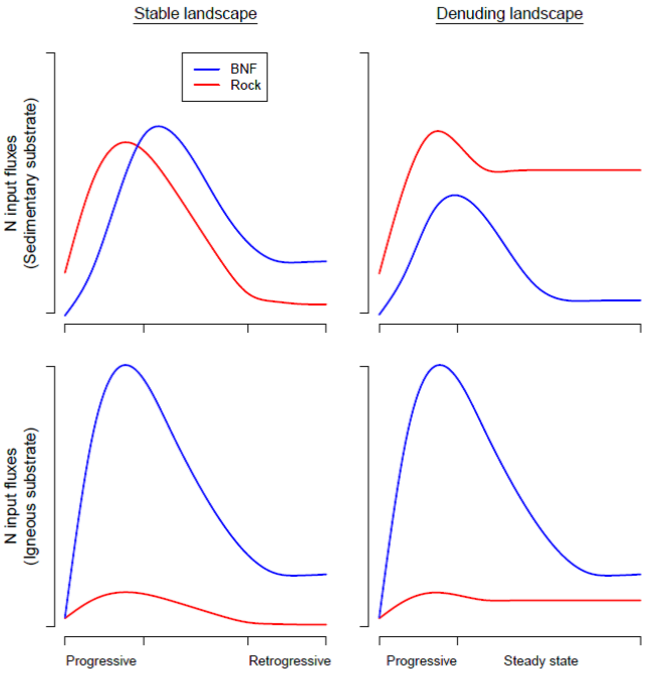

**Figure 7.** Conceptual diagram of interacting state-factor controls (organism, parent material, topography, time) on terrestrial N inputs. The red line is for rock N, the blue line is for biological N fixation (BNF).