



# 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 explicitly considers both rock and atmospheric sources of N. We review evidence for state-factor regulation over biological fixation, deposition, and rock-weathering inputs from local to global scales and in transient vs. steady-state landscapes. Our investigation 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., the 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, non-symmetrical feedbacks among input pathways in which high N inputs via deposition or rock-weathering sources have the potential to reduce biological fixation rates mark N as fundamentally different from other nutrients. The new synthesis for terrestrial N inputs provides a novel set of research issues and opportunities in the multidisciplinary Earth system sciences, with implications for patterns of N limitation, tectonic controls over biogeochemical cycling, and carbon–nutrient–climate interactions.

## 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 via rocks vs. atmospheric sources, as

well as how such inputs vary as a function of soil-forming state factors, including 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 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, defined as the systemic decline in soil fertility and productivity over primary succession, have been observed widely in chronosequence studies across latitudes (Wardle et al., 2004; Peltzer et al., 2010; Izquierdo et al., 2013). This research supports the idea that soils and ecosystems progress interminably toward a state of profound nutrient depletion in the absence of disturbance (Wardle et al., 2004; Vitousek et al., 2010).

More recently, several researchers have shown that the atmosphere is also a source of cations and P, 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), suggesting connections between global atmospheric circulation and patterns of soil fertility (Porder and Hilley, 2011). A recent union of the traditional pedogenic models with landscape principles also shows that erosion can reset 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, 2006). Newer concepts 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 state-factor regulation of ecosystem fertility (Vitousek, 2004), giving rise to a suite of process-based models used to predict P and cation availability in the pedosphere (e.g., Porder and Hilley, 2011).

We suggest that a complementary, new synthesis for terrestrial N cycling could prove equally beneficial. Nitrogen limits terrestrial productivity and microbial functioning in many ecosystems, marking this nutrient as one of the most important and complex biogeochemical cycles on Earth (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008). Conceptual and process-based models of the N cycle are anchored in the idea that this nutrient enters ecosystems solely

from the atmosphere (Delwiche, 1970; Vitousek et al., 1997; Galloway et al., 2004; Ciais et al., 2013; Fowler et al., 2013). Textbook paradigms emphasize biological N fixation (the conversion of  $N_2$  to bioavailable N forms) and atmospheric N deposition inputs to local ecosystem (Bormann and Likens, 1979; Vitousek, 2004) and global N balances (Schlesinger, 1997). 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 process-based 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 et al., 2013).

However, a growing body of evidence suggests that rock weathering has been overlooked as a direct source of N in soils and ecosystems. The largest reservoir of fixed N has accumulated in crustal rocks over deep time, such that > 99 % of Earth's reactive N (N forms other than  $N_2$  gas) now occurs in the geosphere (Schlesinger, 1997). Although much of this N is deep within the crust, rocks have considerable amounts of N, and weathering has been implicated in soil fertility (Strathouse et al., 1980), ecosystem functioning (Dahlgren, 1994; Holloway et al., 1998), and terrestrial C and N storage across an array of ecosystem sites (Morford et al., 2011). Geochemical models have pointed to the importance of N weathering in regulating atmospheric  $N_2$  over deep time (Berner, 2006). The burial of fixed N in marine environments ( $\sim 25 \text{ Tg yr}^{-1}$ ; Gruber and Galloway, 2008) greatly exceeds volcanic degassing ( $\sim 0.4 \text{ Tg yr}^{-1}$ ; Busigny et al., 2011), suggesting that the majority of the N transferred to the crust must be recycled via rock uplift and weathering. This imbalance implies that global rock N inputs may be of a similar magnitude to lower-bound estimates of biological N fixation in natural terrestrial sites ( $58 \text{ Tg yr}^{-1}$ ; Vitousek et al., 2013).

Here, we argue for a new synthesis for terrestrial N inputs that explicitly considers both rock and atmospheric sources of N. We review evidence for atmospheric vs. rock N inputs within the ecosystem state-factors model to address the diversity of N input patterns and magnitudes among Earth's terrestrial environments. We use case studies, consilience, and analogy to develop a novel set of research questions and opportunities. We make reference to elements other than N (i.e., P and cations) to infer likely patterns of rock N weathering inputs where research is less well developed. We also discuss implications of the new synthesis for conceptual nutrient cycling models, terrestrial C storage, patterns of soil fertility, climate change feedbacks, and widespread changes to the global N cycle via human actions.

## 2 Ecosystem state-factor approach

We adopt the classic "state-factor framework" to build toward a more comprehensive understanding of N inputs in ter-

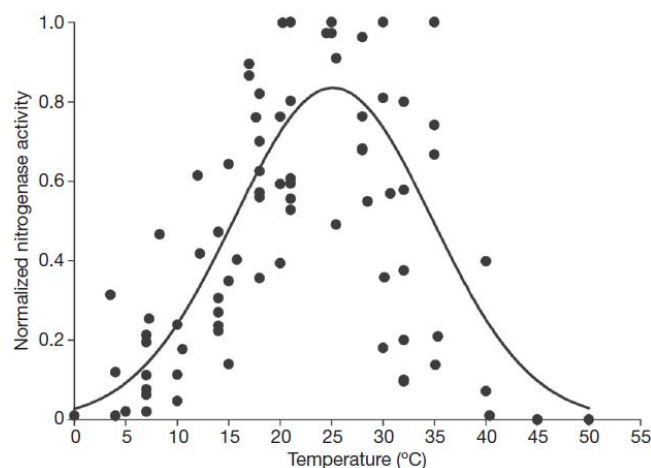
restrial ecosystems. We emphasize regulation, patterns, and interaction of N inputs with soil pattern and process, across local, landscape, and global scales. Our approach takes advantage of Jenny's (1941) system, which has been applied widely to other nutrients (e.g., Vitousek, 2004), wherein five ecosystem state factors are used to understand soil fertility and pedogenic patterns across the Earth system. The five factors are 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; see Vitousek et al. (2002) and Reed et al. (2011) for in-depth reviews on N fixation, Lovett (1994) and Lamarque et al. (2005) regarding N deposition, and Holloway and Dahlgren (2002) regarding rock N chemistry. Instead, 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. We further stress that there are other important approaches beyond those steeped in the tradition of Jenny's framework, particularly the widespread development and application of process-based models in the biogeosciences. We thereby point out several cases in which process-based models have been developed to examine patterns of soil nutrient availability, and how such models both build and advance upon the state-factor assessment herein.

## 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 (including both free-living and symbiotic N fixers), latitudes and soil conditions, in which nitrogenase activity approaches a global maximum at  $\sim 25^{\circ}\text{C}$  (Fig. 1). This temperature falls within the range of 20 to  $30^{\circ}\text{C}$  observed for maximum rates of free-living fixation by soil-crust communities across arctic to tropical climates (Belnap, 2002). Thus, there is little evidence for acclimation of N fixation across biomes, perhaps owing to the complex nature of the nitrogenase enzyme and the high energy costs of fixation (Houlton et al., 2008). The integrated data in Fig. 1 can be fitted to a single Arrhenius function with a slope that falls between the steep temperature dependence of the nitrogenase enzyme and the less pronounced temperature sensitivity of photosynthesis (Houlton et al., 2008).

Knowledge of the climate factors' regulation of fixation has led to the development of several process-based models



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

(Houlton et al., 2008; Wang and Houlton, 2009), thus helping to resolve patterns of terrestrial N fixation that were otherwise considered paradoxical (Jenny, 1950; Crews, 1999). 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 model applications have thus suggested that climate warming could stimulate fixation at high latitudes, whereas low-latitude tropical sites may exhibit declines in this important N input pathway (Wang and Houlton, 2009; Ciais et al., 2013). This implies a strengthening of N limitation in tropical ecosystems and a reduction in future C storage in the highly productivity tropical forest biome.

Similar to N fixation inputs, nutrient weathering inputs are sensitive to the climate factor; however, the water balance of the ecosystem (i.e., precipitation minus evapotranspiration) appears more central to chemical-weathering rates across landscapes than temperature alone (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 wa-

ter 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 arising as a strong control over N weathering inputs to plant–soil systems (Morford, 2014).

## 2.2 Organisms

We suggest that the organism factor plays a direct and indirect role in the pattern and regulation of all three terrestrial N input pathways. The organism 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). Rates of symbiotic N fixation track these global and succession-related abundance patterns (Cleveland et al., 1999; Houlton et al., 2008; 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). This connection is pronounced in desert ecosystems, where patch-scale heterogeneity in soil-crust communities and seasonality in moisture and temperature alter spatial patterns of N fixation and nutrient cycling (Belnap, 2002).

Although the flux of N fixation is notoriously difficult to measure given the large background of atmospheric N<sub>2</sub>, several field studies have found a link between patterns of symbiotic N fixers and N input fluxes in ecosystems. Binkley et al. (1994) reported that populations of *Alnus* sp. symbiotically fix anywhere from 50 to 100 kg N ha<sup>-1</sup> yr<sup>-1</sup> in mixed stands and up to 200 kg N ha<sup>-1</sup> yr<sup>-1</sup> in monodominant 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 of N fixation (~47 kg N ha<sup>-1</sup> yr<sup>-1</sup>) by this species in recently disturbed and riparian zone sites (Hurd et al., 2001), though researchers in Wisconsin reported low rates of N fixation (<5 kg N ha<sup>-1</sup> yr<sup>-1</sup>) 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 ha<sup>-1</sup> yr<sup>-1</sup> (Smithwick et al., 2005). Studies using foliar <sup>15</sup>N/<sup>14</sup>N in arid sites have suggested similarly high rates of N fixation (9 to 22 kg N ha<sup>-1</sup> yr<sup>-1</sup>) in *Prosopis glandulosa* (mesquite) stands (Geesing et al., 2000).

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 (ter Steege et al., 2006), with model-based fluxes suggesting anywhere from 0 to >100 kg N ha<sup>-1</sup> 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 ~5 times and soil inorganic N pools by >3 times in N-limited Hawaiian tropical rainforest. Using process-based modeling and mass-balance approaches, Cleveland et al. (2013) proposed a positive correlation between the abundance of Fabaceae and ecosystem-level N inputs in primary forest sites in central Rondônia of the Amazon Basin.

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). Free-living rates of fixation in rocks and soil are lower than symbiotic ones, but the widespread distribution of cryptogams, and the capacity of such organisms to respond rapidly to change, means that this functional group is globally important, perhaps accounting for up to 50 % of terrestrial N fixation (Elbert et al., 2012). Moreover, spatial coherence between the abundance of fixers and 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, 1993; Vitousek et al., 2002; Reed et al.,

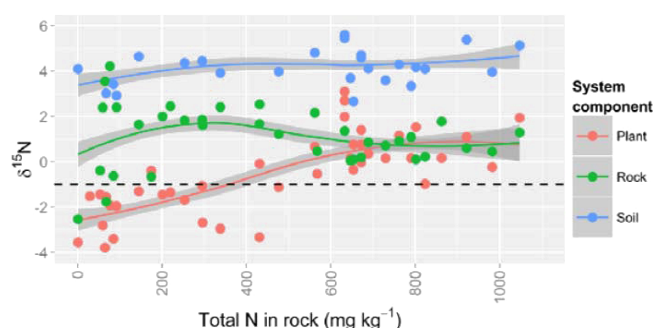


2011). For example, Perakis et al. (2011) demonstrated that high N fixation rates by *Alnus* sp. in early succession resulted in high soil N cycling and availability in non-fixing Douglas fir stands for decades. This kind of temporal dynamism, in which fixers are long since absent from sites where fixation 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).

In addition to direct effects, an important indirect role of the organism factor is apparent in atmospheric N inputs. Nitrogen inputs rates via dry deposition and cloud water are affected by community composition and forest structure (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). An extensive study in Europe reported N throughfall fluxes under conifer canopies that exceeded bulk N deposition rates by a factor of  $\sim 4$  (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. This occurs through direct and indirect mechanisms mediated by plant-microbe interactions. “Rock-eating fungi” have been shown to directly accelerate the weathering of calcium ( $\text{Ca}^{2+}$ )- and potassium ( $\text{K}^+$ )-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, such as succinate, citrate, oxalate, formate, and malate (Jongmans et al., 1997; Hoffland et al., 2004; van Scholl et al., 2006, 2008). Other mechanisms include the production of siderophores, particularly via ectomycorrhizae (ECM), which bind iron and thereby accelerate soil mineral weathering and horizon development (Taylor et al., 2009). Indirectly, biomass allocations to belowground root and hyphal networks increase reactive mineral surfaces, provide C for microbial decomposition, and contribute to increased soil acidity. Together, these factors are thought to 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  $\text{CO}_2$  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 sug-



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

gests that N can be directly transferred from rocks to plants in ecosystems, which might be mediated by fungal mutualism (Fig. 2). The isotopic composition ( $\delta^{15}\text{N}$ ) of rock N sources (green line) is on average higher than atmospheric N inputs (Holloway and Dahlgren, 2002; Houlton and Bai, 2009), which are typically between 0 and  $-3\text{‰}$  (dashed line). Across a set of temperate forest sites dominated by Douglas fir, the  $\delta^{15}\text{N}$  of foliage converges on that of rock  $\delta^{15}\text{N}$  when rock concentrations exceed  $\sim 500\text{ ppm N}$ ; however, soil  $\delta^{15}\text{N}$  is consistently higher than rocks and other N input pathways as the result of fractionating losses (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.

### 2.3 Topography

Topographic gradients regulate erosion and chemical-weathering rates; thus, this factor affects N fixation (discussed in “Parent material” section below) and could strongly affect rock N inputs to soil. At large scales, erosion rates are strongly correlated with topographic relief (Montgomery and Brandon 1994; Portenga and Bierman 2011), and 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 treated as the balance between uplift and erosion, with active orogens representing potential “hotspots” 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 and theoretical models show that chemical weathering is maximized in landscapes with moderate to high erosion owing to the rapid exhumation of fresh reactive minerals (Stallard and Edmond, 1983; Riebe

et al., 2004; West et al., 2005; Gabet and Mudd, 2009). 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) suggests that rock-derived nutrient availability ought to peak at moderate uplift rates, where the ratio of weathering inputs to losses reaches a global maximum. Within 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, which limits 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). Similarly, rock N inputs in low-relief landscapes are expected to be substantially lower than moderate- to high-relief environments owing primarily to low rates of rock exhumation and denudation. The development of thick zones of saprolite/regolith weathering in some low-relief landscapes may also result in rock N weathering at depth within the critical zone, beyond the reach of plant life.

At local scales, erosion and soil production (conversion of rock to soil) are proportional to slope and linearly correlated with the negative curvature of topography (Heimsath et al., 1997; Roering et al., 1999). Both weathering rates and erosion in hillslope sequences are generally highest at convex positions near ridgetops (i.e., shoulder positions), contributing to accumulation of weathering products in concave positions lower in the landscape (i.e., 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 hillslope summit positions are variable and slope-dependent, but when these positions are flat and non-eroding (i.e., stable geomorphic surfaces), 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 unweathered 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  $^{15}\text{N}/^{14}\text{N}$  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 Smoky Mountains (Garten and Vanmiegroet, 1994). Likewise, total soil N concentrations were elevated in shoulder positions of cante-nae 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 to 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

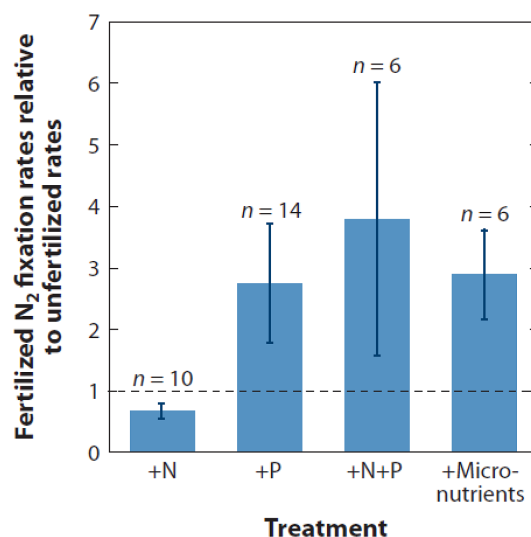
We suggest that the parent material factor regulates patterns and rates of N fixation and rock input pathways. Rocks contain ~99 % of Earth's fixed N (Schlesinger, 1997), even when excluding mantle reservoirs that interact sparingly with Earth surface processes (Bebout et al., 2013). Approximately 75 % of the fixed N reservoir within the continental crust is found in sedimentary and metasedimentary rocks (Goldblatt et al., 2009), which primarily reflects higher rates of N fixation compared to denitrification over Earth's history. Nitrogen concentrations are much higher in sedimentary/metasedimentary 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 ammonium, 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 diagenesis in sedimentary basins, 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. Generally, N enrichment is highest among fine-grained siliciclastic rocks (i.e., shales, mudstones) and their low-grade metamorphic counterparts (i.e., slate, phyllite, and mica-schist). These rocks comprise  $\sim 30\%$  of Earth's continental surfaces and have an average N concentration equal to  $700\text{--}1000\text{ mg N kg}^{-1}$  (Durr et al., 2005; Goldblatt et al., 2009; Morford, 2014).

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 Californian 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 concentrations to variations in 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 unvegetated sites in northern California; rapid N release from rock minerals stimulated soil nitrification rates and the production of  $\text{H}^+$ , which in turn elevated labile Al concentrations in mountaintop barrens (Dahlgren, 1994). In contrast, the nearby vegetated sites stored  $\sim 50\%$  more C and N in soils compared to N-poor dioritic sites, with N weathering inputs more than doubling terrestrial N balances compared to atmospheric N inputs alone (Morford et al., 2011). The effect of N-rich rocks on terrestrial C storage was apparent in forest biomass across the Pacific Northwest, suggesting largely beneficial effects of bedrock N on soil fertility and  $\text{CO}_2$  uptake at regional scales.

The parent material factor also controls atmospheric N inputs. In particular, biological N fixation responds to changes in trace metals (e.g., molybdenum (Mo)) and P, owing to the biochemical demands of nitrogenase, high adenosine triphosphate (ATP) requirements of N fixation, 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 these elements can substantially limit fixation in both symbiotic

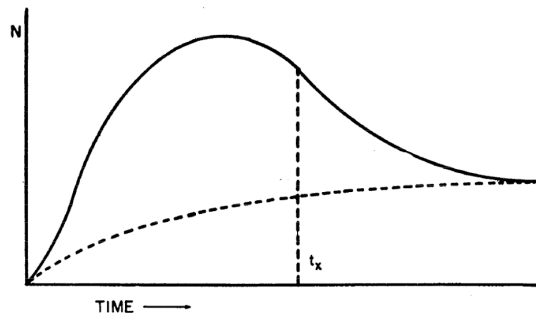


**Figure 3.** Response of free-living N fixation rates to different nutrient fertilization treatments. Values above 1 on the y axis indicate positive response, while those below indicate a negative response to fertilization by +N, +P, +N+P, or +micronutrients (from Reed et al., 2011).

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 shows that rock P chemistry controls 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 additions (Wurzburger et al., 2012).

## 2.5 Time

Here we emphasize the time factor over primary succession where new ecosystems develop from 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 pedogenesis. This is especially clear in sites where other N inputs are low – a condition that would seem to confer 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 out-compete 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; Vi-



**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 depicts cases where fixers are absent from early successional sites (from Jenny, 1958).

tousek 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 III et al., 1994), cyanolichens are among the earliest colonizers, with direct and indirect evidence for significant free-living N fixation rates in fresh parent material (Schlesinger et al., 1998; Crews et al., 2001). These pioneering species produce the N that facilitates 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 III et al., 1994, 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 III 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 fine-scale soil heterogeneity 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  $\sim 11 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  until  $> 60$  years of pedogenesis. Thereafter, this species was competitively excluded from older sites along the Franz Josef chronosequence 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-

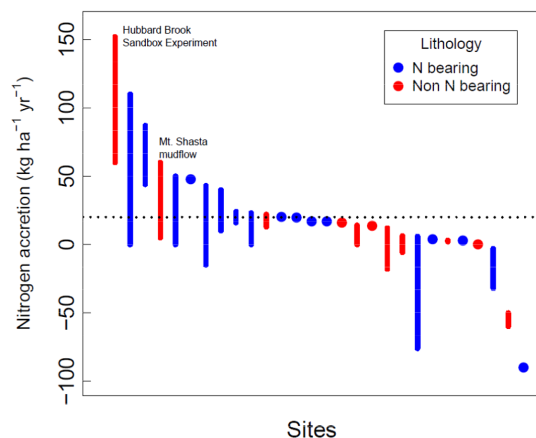
living paths along the Hawaii chronosequence (Matzek and Vitousek, 2003). Furthermore, work on free-living fixation in the boreal suggests a pattern that opposes Jenny's (1958) model: rates of N fixation in feather moss communities have been shown to increase over primary succession, likely in response to declines in N availability over time (Zackrisson et al., 2004).

Therefore, a key implication of past research is that average soil nutrient conditions do not necessarily impose controls 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 the canopy environment, 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 cyanolichen 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, direct knowledge of rock N inputs during primary succession is sparse. Rather than measuring and examining the potential for rock weathering to alter N inputs over succession, most studies assume that rock N inputs are uniformly unimportant in newly formed ecosystems (sensu Walker and Syers, 1976). This assumption is probably true for igneous substrates (e.g., Hawaii chronosequence; Vitousek, 2004), where parent material N contents are typically low (Holloway and Dahlgren, 2002), but not for many sedimentary and metasedimentary substrates (see also "Parent material" section above).

Binkley et al. (2000) analyzed evidence for surprisingly high rates of N accumulation in terrestrial ecosystems. Their assessment placed high confidence in the results for N accumulation (soil plus vegetation) rates observed for forests in Walker Branch, Tennessee ( $> 43$  to  $70 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) (Johnson and Todd, 1998), where the lithology is dominated by differential sequences of marine carbonate and siliciclastic sediments. A closer inspection of N accretion studies (Binkley et al., 2000; Johnson and Turner, 2014) reveals that 8 of the 10 temperate sites with unusually high N accumulation rates (i.e.,  $> 20 \text{ kg ha yr}^{-1}$ ) were from sites with high geologic N input capacities (see Table in the Supplement; 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 and N-poor geologic substrates; however, nearly all the studies reporting high N accumulation rates come from sites on sedimentary parent materials (Fig. 5). This data reanalysis provides testable evidence for





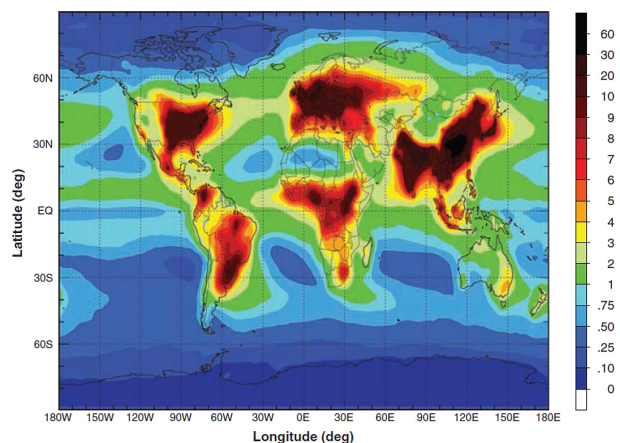
**Figure 5.** Nitrogen accumulation rates in terrestrial ecosystems underlain by N-bearing vs. non N-bearing lithologies. The dashed line is the cutoff for rates of N accumulation that exceed estimates of atmospheric N inputs (i.e.,  $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ). See supplemental table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

rock N sources in the “missing N inputs” across a range of temperate forest sites.

## 2.6 Anthropogenic

Humans have become the single-greatest force in terrestrial N inputs. Agricultural expansion, synthetic fertilizer production, and fossil fuel combustion have doubled the amount of reactive N circulating in the terrestrial biosphere (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, whereas rock-mining activities have mobilized geological N, but not in a way that has greatly changed N inputs to natural sites. Further, human alterations 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 airborne agricultural losses of N. From a global budget perspective, agricultural emissions of  $\text{NO}_x$  and  $\text{NH}_3$  comprise a large-scale recycling term, despite representing a new N input to downwind ecosystems.

Hence, the anthropogenic factor has clearly altered patterns of N deposition in natural and unmanaged soil systems worldwide (Holland et al., 1997; Lamarque et al., 2005). Prior to widespread human activities, a small amount ( $\sim 5$  to  $10 \text{ Tg N yr}^{-1}$ ) of N was fixed during lightning strikes and washed out of the atmosphere. The airborne sources of N through human activities have greatly changed patterns of N deposition inputs from the preindustrial state, so that modern rates of N deposition correspond with areas of fertilizer use and industrialization (Fig. 6). Current estimates suggest that  $\sim 30\%$  of anthropogenic N deposition is derived from



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

fertilizers, with the majority (i.e., 70 %) derived from mobile and stationary fossil fuel sources (Schlesinger, 2009). Whereas the largest postindustrial 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 subtropical 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). The implications of anthropogenic N deposition are far-reaching and widespread and underlie a host of land, air, and water quality issues (Vitousek et al., 1997; Houlton et al., 2013).

## 3 Discussion and implications

We propose a new synthesis for terrestrial N inputs that explicitly considers both atmospheric and rock sources of N. The state-factor analysis we adopt complements our understanding of controls on P and cation availability in soil, and so it offers a common and historically robust system against which the major element cycles can be examined. We view our synthesis as a point of departure: we provide a broad list of controls over the most substantial state-factor effects on terrestrial N input patterns and magnitudes, with explicit corollaries for each factor summarized in Table 1. Understanding the new synthesis for terrestrial N inputs across diverse soil and ecosystem conditions is important for three principal reasons.

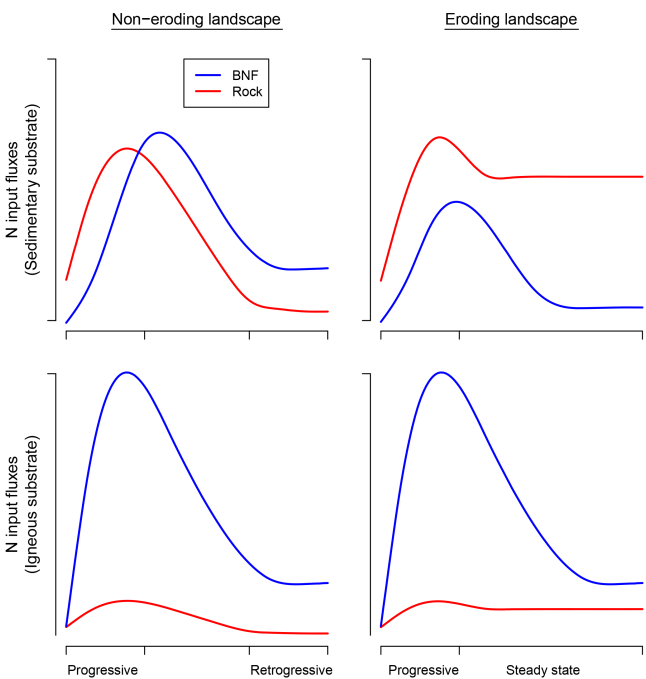
First, N limitation to terrestrial plant productivity and microbial functioning is widespread (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008), yet questions remain over the reasons for this biogeochemical phenomenon. Whether N limitation is transient or sustained is largely determined by the magnitude of N inputs, their spatial variation, and their relationship to N losses to erosion, the hydrosphere, and the atmosphere (Hedin et al., 1995; Vitousek et al., 2002;

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

State factor	Biological N <sub>2</sub> fixation	N deposition	N chemical weathering
Climate	Generally increase with temperature; global optimum ~ 25°C	–	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	–

Houlton et al., 2003; Houlton and Bai, 2009; Cleveland et al., 2013). The new synthesis that considers both rock and atmospheric N sources, and how such sources are regulated by state factors and biogeochemical processes, 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), and do not reveal controls on nutrient limitation patterns. Knowledge of how state factors are likely to shape the sources of N that dominate among different biogeochemical environments will improve our understanding of the causes and consequences of terrestrial N limitation.

Second, explicit consideration of rock and atmospheric N sources will improve our understanding of terrestrial ecosystem feedbacks on climate change. Global biogeochemical projections that consider N availability point to much less CO<sub>2</sub> capture and soil C sequestration than those without an N cycle (Hungate et al., 2003; Thornton et al., 2007; Wang and Houlton, 2009; Zaehle et al., 2010a). The recent IPCC AR5 included only one N cycle model that, when coupled to two different Earth system models (ESMs), suggested less CO<sub>2</sub> uptake and more climate warming than model simulations in the absence of N limitation (Ciais et al., 2013). The uncertainty in terrestrial N input paths and C by N interactions could result in up to 2 °C of additional warming by 2100 (Wang and Houlton, 2009). However, none of these models have considered N inputs via rock sources or the potential for this N input path to alter patterns of ecosystem N and C storage (e.g., Morford et al., 2011). The new synthesis argues for important controls over rock N inputs in all but one (i.e., 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, but most clearly in the case of



**Figure 7.** Conceptual diagram of interacting state-factor controls (organism, parent material, topography, time) on terrestrial N inputs (biological N fixation (BNF) and rock weathering). Our synthesis points to sustained and ecologically significant rock N inputs among eroding landscapes with high N parent material (e.g., fine-grained sedimentary rocks). Among non-eroding landscapes, rock N inputs may be high when fresh bedrock is exposed but otherwise comprise a small fraction of the long-term N input.

rock N weathering and biological N fixation inputs (Table 1).

Third, conceptual models based on the new synthesis will advance our understanding of variation in soil N fertility and enrich modern nutrient cycling concepts (Fig. 7). Pedogenic models have assumed that fixation and deposition can al-

ter patterns of ecosystem development but have hitherto neglected rock N sources (Walker and Syers, 1976). By separating the parent material factor between N-poor and 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, and 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 N inputs within individual state factors, N source pathways are likely to affect one another within a given state-factor setting. For example, theory and experimental research demonstrate that external N inputs reduce the capacity for terrestrial N fixation (Vitousek et al., 2002; Reed et al., 2011; Fig. 3). This dynamic occurs 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 inputs with high N / P could reduce rates of fixation in a given soil system, all else remaining equal. Alternatively, given plant-litter controls on free-living N fixation rates (Vitousek and Hobbie, 2000), it is possible for fixation along free-living paths to increase in high rock N input sites. If plant litter quality increases in response to high rock N inputs, free-living rates of N fixation could increase rather than decrease.

Indeed, that biological N fixation can respond rapidly to changes in N input pathways is what marks N as fundamentally different from all other biogeochemical cycles (Vitousek et al., 2010). Phosphorus, cations, and essential trace metals can be derived from atmospheric deposition, dust, and rock weathering, yet they lack important gaseous phases and an N fixation analogue to promote rapid feedback among 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 biological N fixation, in contrast to state-factor controls over other soil elements in which input sources are not directly tied to one another.

The state-factor approach we adopt provides testable predictions for the new synthesis, but it by no means should be taken as the only approach to understanding atmosphere, biosphere, and geosphere effects on the N cycle. We view the state-factor model as a powerful and proven integrative tool that offers useful sets of concepts to help guide experimental research in the Earth system sciences. It is historically important to soil and ecosystem science and, in the case of N, places this element in a similar construct with the traditional rock-derived elements. The weakness of the state-factor approach lies in the lack of quantitative predictions of N input kinetics and the absence of focus on individual processes. We suggest that process-based model development should go hand in hand with state-factor approaches in developing the new synthesis. This approach has proven quite effective for understanding weathering of the traditional rock-derived elements. For example, work along a set of chronosequences has been used to develop process-based models and quantitative predictions of P inputs and limitation patterns globally (Porder and Hilley, 2011). We envision that parallel activities – in which state-factor assessments are combined with an examination of reaction kinetics, particularly N fixation and N weathering kinetics in controlled settings – can give rise to a more general understanding of N input pathways and magnitudes. Experiments designed to evaluate the kinetics of chemical weathering vs. physical erosion will be particularly important to determining the availability of rock N sources to terrestrial biota.

The new synthesis has implications for many different aspects of global environmental change. 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. 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). However, patterns of N saturation have been difficult to understand, and could be affected by the amount of rock N weathering inputs in different ecosystems (Dahlgren, 1994). In contrast, 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). Research on progressive N limitation has been mixed, and could be affected by all three N input pathways, with evidence for rock N inputs substantially altering the C sink capacity of forest ecosystems (Morford et al., 2011). A greater appreciation of the pattern, magnitude, and response of atmospheric vs. rock N inputs will go a long way toward understanding changes to Earth's diverse soils, landscapes, and ecosystems in the Anthropocene.

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