

1 **A new synthesis for terrestrial nitrogen inputs**

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18 **Abstract**

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

40 from other nutrients. The new synthesis for terrestrial N inputs provides a novel set of research  
41 issues and opportunities in the multi-disciplinary Earth system sciences, with implications for  
42 patterns of N limitation, tectonic controls over biogeochemical cycling, and global carbon-  
43 nutrient-climate interactions.

44 **Keywords:** State-factors; deposition; fixation; weathering; global change; geobiology; nutrient  
45 limitation

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57 **1. Introduction**

58           Nutrients have a long-standing and demonstrated importance in the pattern and  
59 regulation of soil-systems, their services, and their functioning across Earth's diverse  
60 environments. An extensive literature has been developed around the concept that biologically  
61 essential elements, particularly nitrogen (N) and phosphorus (P), influence patterns of plant  
62 productivity, biodiversity and soil carbon (C) contents from temperate to tropical biomes  
63 (Jenny, 1980; Vitousek, 1984; Vitousek and Howarth, 1991; McGroddy et al., 2004; Elser et al.,  
64 2007; Cleveland et al., 2013; Fernández-Martínez et al., 2014). Classical soil paradigms have  
65 focused on primary nutrient input paths via rocks vs. atmospheric sources, and how such inputs  
66 vary as a function of soil-forming state factors, including time, parent material, biota, climate,  
67 and topographic relief (Jenny, 1941). New nutrient inputs are necessary for the maintenance of  
68 soil fertility, rejuvenating persistent ecosystem losses to erosion, leaching and the atmosphere  
69 (Schlesinger and Bernhardt, 2013). The demonstrative importance of nutrient input principles is  
70 therefore embedded in seminal work by Walker and Syers, Jenny, and Vitousek and colleagues,  
71 making a substantial contribution to environmental soil science, ecology, biogeochemistry and  
72 global change.

73           Traditional concepts have argued for age-related declines in nutrient inputs via rock  
74 weathering sources over the long-term course of pedogenesis. While fresh parent material is  
75 often high in P and cations, Walker and Syers (1976) suggested that weathering and erosion  
76 deplete these elements in primary substrates, with progressive P occlusion into biologically  
77 unavailable pools over millions of years of ecosystem development. Work by Jenny et al. (1969)  
78 in the Mendocino terraces has led to the concept of the terminal steady-state in stable

79 landforms in which rock weathering inputs cease and profound P-depletion results in severe  
80 stunting of forest vegetation over millennia (Izquierdo et al., 2013). Vitousek and Farrington  
81 (1997) used direct fertilization experiments to show that P becomes progressively limiting to  
82 terrestrial productivity in old Hawaiian sites, following long-term declines in soil P availability in  
83 highly weathered volcanic soils (Crews et al., 1995). These patterns of retrogression, defined as  
84 the systemic decline in soil fertility and productivity over primary succession, have been  
85 observed widely in chronosequence studies across latitudes (Wardle et al., 2004; Peltzer et al.,  
86 2010; Izquierdo et al., 2013). This research supports the idea that soils and ecosystems progress  
87 interminably toward a state of profound nutrient depletion in absence of disturbance (Wardle  
88 et al., 2004; Vitousek et al., 2010).

89         More recently, several workers have shown that the atmosphere is also a source of  
90 cations and P, with landscape scale features altering the trajectory of soil development  
91 compared to flat stable surfaces in highly weathered landscapes. Work in highly weathered  
92 tropical sites demonstrates the importance of long-distance dust transport in sustaining soil P  
93 and cation fertility (Chadwick et al., 1999), suggesting global-scale connections between dust  
94 transport, climate change, and soil fertility (Porder and Hilley, 2011). A recent union of the  
95 traditional pedogenic models with landscape principles also shows that erosion can re-set the  
96 clock of ecosystem development, such that rock-derived elements can once again play a  
97 substantial role in otherwise highly weathered and P-limited ecosystems (Vitousek et al., 2003;  
98 Porder et al., 2005; Porder et al., 2006). Newer concepts have thereby been devised to explicitly  
99 address controls of tectonic uplift, erosion, climate, time and atmospheric transport on  
100 patterns of P, silicon (Si) and cation inputs to soil (Okin et al., 2004; Vitousek, 2004; Hilley and

101 Porder, 2008; Mahowald et al., 2008; Hartmann et al., 2014). This growing appreciation for  
102 atmospheric and rock sources has substantially enriched our understanding of state-factor  
103 regulation of ecosystem fertility (Vitousek 2004), giving rise to a suite of process-based models  
104 used to predict P and cation availability in the pedosphere (e.g., Porder and Hilley, 2011).

105         We suggest that, a complementary, new synthesis for terrestrial N cycling could prove  
106 equally beneficial. Nitrogen limits terrestrial productivity and microbial functioning in many  
107 ecosystems, marking this nutrient as one of the most important and complex biogeochemical  
108 cycles on Earth (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008). Conceptual and  
109 process-based models of the N cycle are anchored in the idea that this nutrient enters  
110 ecosystems solely from the atmosphere (Delwiche, 1970; Vitousek et al., 1997; Galloway et al.,  
111 2004; Ciais, 2013; Fowler et al., 2013). Textbook paradigms emphasize biological N fixation (the  
112 conversion of N<sub>2</sub> to bio-available N forms) and atmospheric N deposition inputs to local  
113 ecosystem (Bormann and Likens, 1979; Vitousek, 2004) and global N balances (Schlesinger,  
114 1997). Controls on fixation and deposition have been examined and discussed extensively  
115 (Vitousek et al., 2002; Galloway et al., 2004; Lamarque et al., 2005; Reed et al., 2011), and  
116 process-based models have accounted for these N inputs in climate change and global carbon  
117 storage projections (Thornton et al., 2007; Wang and Houlton, 2009; Zaehle et al., 2010b; Ciais,  
118 2013).

119         However, a growing body of evidence suggests that rock weathering has been an  
120 overlooked as a direct source of N to soils and ecosystems. The largest reservoir of fixed N has  
121 accumulated in crustal rocks over deep time, such that >99% of Earth's reactive N (N forms  
122 other than N<sub>2</sub> gas) now occurs in the geosphere (Schlesinger, 1997). Although much of this N is

123 deep within the crust, various different rocks have considerable amounts of N, and weathering  
124 has been implicated in soil fertility (Strathouse et al., 1980), ecosystem functioning (Dahlgren,  
125 1994; Holloway et al., 1998), and terrestrial C storage and N across an array of ecosystem sites  
126 (Morford et al., 2011). Geochemical models have pointed to the importance of N weathering in  
127 regulating atmospheric N<sub>2</sub> over deep time (Berner, 2006). The burial of fixed N in marine  
128 environments (~25 Tg yr<sup>-1</sup>, Gruber and Galloway, 2008 ) cannot be compensated by solely  
129 volcanic degassing (~ 0.4 Tg yr<sup>-1</sup>, Busigny *et al.* 2011), suggesting that the majority of the N  
130 transferred to the crust must be recycled via rock uplift and weathering. This implies that global  
131 rock N inputs may be of similar magnitude to lower-bound estimates of biological N fixation in  
132 natural terrestrial sites (58 Tg yr<sup>-1</sup>, Vitousek et al. 2013).

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

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## 144 **2. Ecosystem State-factor approach**

145           We adopt the classic “state-factor framework” to build toward a more comprehensive  
146 understanding of N inputs in terrestrial ecosystems. We emphasize regulation, pattern and  
147 interaction of N inputs with soil pattern and process, across local, landscape and global scales.  
148 Our approach takes advantage of Jenny’s system (1941), which has been applied widely to  
149 other nutrients (e.g., Vitousek, 2004), wherein five ecosystem state-factors are used to  
150 understand soil fertility and pedogenic patterns across the Earth system. The five factors  
151 include parent material, climate, organisms, topography (or relief) and time (Jenny 1941). In  
152 addition, given the importance of human actions on Earth’s biogeochemistry, we include an  
153 anthropogenic factor in our analysis here, consistent with previous calls for this sixth factor  
154 (Amundson and Jenny, 1991).

155           Our review is not necessarily deep into any given N input path; for in-depth reviews on  
156 N fixation see Vitousek et al. (2002) and Reed et al. (2011); N deposition see Lovett (1994) and  
157 Lamarque et al. (2005); and rock N chemistry see Holloway and Dahlgren (2002). Instead, our  
158 aim is to examine how different state factors broadly influence the distribution and magnitude  
159 of atmospheric vs. rock N sources, with case studies presented throughout our synthesis. We  
160 further stress that there are other important approaches beyond those steeped in the tradition  
161 of Jenny’s framework, particularly the widespread development and application of process-  
162 based models in the biogeosciences. We thereby point out several cases in which process-  
163 based models have been developed to examine patterns of soil nutrient availability, and how  
164 such models both build and advance upon the state-factor assessment herein.

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167 **2.1 Climate**

168 Climate is among the chief regulators of terrestrial N input paths and magnitudes,  
169 particularly N fixation and rock weathering sources across soil-systems. Biological N fixation is  
170 mediated by nitrogenase, an enzyme which exhibits a steep temperature-dependency and high  
171 activation energy (Cueterick et al. 1978). A global compilation of data has revealed that the  
172 effect of temperature on N fixation is apparent across a range of organisms (including both  
173 free-living and symbiotic N fixers), latitudes and soil conditions, in which nitrogenase activity  
174 approaches a global maximum at ~25 degrees centigrade (Fig. 1). This temperature falls within  
175 the range of 20 to 30 degrees centigrade observed for maximum rates of free-living fixation by  
176 soil-crust communities across arctic to tropical climates (Belnap, 2002). Thus, there is little  
177 evidence for acclimation of N fixation across biomes, perhaps owing to the complex nature of  
178 the nitrogenase enzyme and the high energy costs of fixation (Houlton et al. 2008). The  
179 integrated data in Fig. 1 can be fitted to a single Arrhenius function with slope that falls  
180 between the steep temperature-dependence of the nitrogenase enzyme and the less  
181 pronounced temperature sensitivity of photosynthesis (Houlton et al. 2008).

182 Knowledge of the climate-factors' regulation of fixation has led to the development of  
183 several process-based models (Houlton et al., 2008; Wang and Houlton, 2009), thus helping to  
184 resolve patterns of terrestrial N fixation that were otherwise considered paradoxical (Jenny,  
185 1950; Crews, 1999). Symbiotic N fixing trees are absent from many high latitude sites, despite  
186 the preponderance of evidence for substantial N limitation in many temperate and boreal  
187 forests (Crews 1999). In contrast, putative fixers in the Fabaceae family (i.e., legumes) are  
188 abundant in lowland tropical forests and savanna ecosystems where several metrics point to an

189 abundance of N (Martinelli et al., 1999; Hedin et al., 2009). Consideration of the climate-factor  
190 helps explain this pattern: temperature limits rates of fixation at higher latitudes where  
191 energy/C is limiting, effectively increasing the C cost of fixation beyond its manifold benefits for  
192 organism functioning (Houlton et al. 2008). Global model applications have thus suggested that  
193 climate warming could stimulate fixation at high latitudes, whereas low-latitude tropical sites  
194 may exhibit declines in this important N input pathway (Wang and Houlton, 2009; Ciais, 2013).  
195 This implies a strengthening of N limitation in tropical ecosystems and reduction in future C  
196 storage in the highly productivity tropical forest biome.

197         Similar to N fixation inputs, nutrient weathering inputs are sensitive to the climate  
198 factor; however, the water balance of the ecosystem (i.e., precipitation - evapotranspiration)  
199 appears more central to chemical weathering rates across landscapes than temperature alone  
200 (Kump et al., 2000; Chadwick et al., 2003). Excess moisture increases the volume of water  
201 moving through soil and rock pores and accelerates mineral dissolution. While temperature is a  
202 primary factor in kinetic models of mineral dissolution (Lasaga et al., 1994), direct temperature  
203 effects may be attenuated by pore water residence time (i.e. fluid flow) in most soils in practice  
204 (Maher, 2010). Indirectly, temperature alters ecosystem water balances by influencing  
205 evapotranspiration, water phase and biological activity, but these effects have been difficult to  
206 disentangle in the field (Amundson et al., 2007).

207         Field-derived weathering rates generally increase across climatic-gradients. Catchment  
208 scale silica fluxes (White and Blum, 1995) and soil clay content (Jenny, 1941) are positively  
209 correlated with increasing temperature plus precipitation. Further, investigations of soil  
210 climosequences show that soil development and weathering rates are maximized in warm and

211 wet sites (Dahlgren et al., 1997; Egli et al., 2003; Rasmussen et al., 2007; Williams et al., 2010).  
212 However, the temperature-sensitivity of weathering has been difficult to isolate in field  
213 settings, and appears to vary as a function soil water-balance (Rasmussen et al., 2011) and/or  
214 biological factors (Riebe et al., 2004). Particularly for biologically important elements (P,  
215 nutrient cations), the temperature sensitivity of field-derived weathering rates may be  
216 substantially lower than laboratory-derived activation energy estimates. This could explain why  
217 observations for soil P weathering rates are commonly more sensitive to precipitation than  
218 temperature (Smeck, 1973; Birkeland et al., 1989; Porder and Chadwick, 2009). Rates of rock N  
219 weathering are similarly affected by climate; high N weathering rates are seen in warm/moist  
220 environments, with the ecosystem water balance arising as a strong control over N weathering  
221 inputs to plant-soil systems (Morford, 2014).

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## 223 **2.2 Organisms**

224 We suggest that the organism factor plays a direct and indirect role in the pattern and  
225 regulation of all three terrestrial N input pathways. The organism factor is self-evident and  
226 direct in the case of N fixation; the presence of organisms with the capacity to fix N is requisite  
227 to this input path, though legacy effects that play out in slowly cycling soil N pools can obscure  
228 the link between fixer populations and N input-output balances in modern ecosystems (e.g.,  
229 (Perakis et al., 2011). Globally, organisms with the capacity to fix N symbiotically are much  
230 more abundant in tropical than temperate forests (Crews, 1999; Menge et al., 2014), with  
231 evidence for increased rates of N fixation following disturbance (i.e., forest gaps) in many  
232 ecosystems (Binkley et al., 1994; Rastetter et al., 2001; Vitousek et al., 2002; Davidson et al.,

233 2007; Davidson, 2008; Barron et al., 2011; Batterman et al., 2013). Rate of symbiotic N fixation  
234 track these global abundance and succession-related abundance patterns (Cleveland et al.,  
235 1999; Houlton et al., 2008; Vitousek and Field, 1999; Smithwick et al., 2005). Further, studies of  
236 N-fixing gene abundance (*nifH*) in the soil have demonstrated a high degree of correlation  
237 between free-living microbial fixers and N fixation rates in ecosystems (Reed et al. 2011). This  
238 connection is pronounced in desert ecosystems where patch-scale heterogeneity in soil-crust  
239 communities and seasonality in moisture and temperature alter spatial patterns of N fixation  
240 and nutrient cycling (Belnap, 2002).

241         Although the flux of N fixation is notoriously difficult to measure given the large  
242 background of atmospheric N<sub>2</sub>, several field studies have found a link between patterns of  
243 symbiotic N fixers and N input fluxes in ecosystems. Binkley et al. (1994) reported that  
244 populations of *Alnus sp.* symbiotically fixes anywhere from 50 to 100 kg N/ha/yr in mixed  
245 stands and up to 200 kg N/ha/yr in mono-dominant ones, with relatively persistent rates where  
246 this species was present in Pacific Northwest sites. Studies in the Adirondack Mountains in New  
247 York found evidence for high rates N fixation (~47 kg N/ha/yr) by this species in recently  
248 disturbed and riparian zone sites (Hurd et al., 2001), though workers in Wisconsin reported low  
249 rates of N fixation (< 5 kg N/ha/yr) by *Alnus sp.* across a range of stand conditions (Younger and  
250 Kapustka, 1983). Where *Ceanothus sp.* is present in early to mid-successional forest sites,  
251 typically following fire, this species has been shown to fix anywhere from 4 to >100 kg N/ha/yr  
252 (Smithwick et al., 2005). Studies using foliar <sup>15</sup>N/<sup>14</sup>N in arid sites have suggested similarly high  
253 rates of N fixation (9 to 22 kg N/ha/yr) in *Prosopis glandulosa* (mesquite) stands (Geesing et al.,  
254 2000).

255 Jenny (1950) suggested that unexpectedly high soil N pools in many lowland tropical  
256 sites reflected the presence of symbiotic N fixers within this biome, an idea that has been  
257 confirmed by some (Batterman et al., 2013) though not all studies in lowland tropical forests  
258 (Vitousek et al., 2002; Barron et al., 2011; Sullivan et al., 2014b). Indeed, legume populations  
259 vary markedly within the Amazon basin (ter Steege et al., 2006), with model-based fluxes  
260 suggesting anywhere from zero to >100 kg N/ha fixed via symbiotic pathways within this  
261 expansive ecosystem (Wang and Houlton, 2009). Moreover, Vitousek et al. (1987)  
262 demonstrated a strong link between the organism factor and N inputs in their study of *Myrica*  
263 *faya*, an invasive fixer that increased N inputs by ~5 times and soil inorganic N pools by >3 times  
264 in N-limited Hawaiian tropical rainforest. Using process-based modeling and mass-balance  
265 approaches, Cleveland et al. (2013) proposed a positive correlation between the abundance of  
266 Fabaceae and ecosystem-level N inputs in primary forest sites in central Rondonia of the  
267 Amazon Basin.

268 The general consensus from these studies is that the presence of fixers points to N  
269 fixation input capacity, though nodulation is a species-dependent property that varies across  
270 ecosystem conditions (Sylvester-Bradley et al., 1980; Sprent and Raven, 1985). Free-living rates  
271 of fixation in rocks and soil are lower than symbiotic ones, but the widespread distribution of  
272 cryptograms, and the capacity of such organisms to respond rapidly to change, means that this  
273 functional group is globally important, perhaps accounting for up to 50% of terrestrial N fixation  
274 (Elbert et al., 2012). Moreover, spatial coherence between the abundance of fixers and rates of  
275 soil N accumulation is not always apparent owing to a host of localized controls and temporal  
276 dynamics in the N fixation process (Walker et al. 1993; Vitousek et al. 2002; Reed et al. 2011).

277 For example, Perakis et al. (2011) demonstrated that high N fixation rates by *Alnus sp.* in early  
278 succession resulted in high soil N cycling and availability in non-fixing Douglas fir stands for  
279 decades. This kind of temporal dynamism, in which fixers are long-since absent from sites  
280 where fixation inputs were high, continues to challenge our ability to address relationships  
281 between terrestrial N fixation, soil N fertility, and ecosystem N losses (Hedin et al., 2009;  
282 Perakis et al., 2011).

283 In addition to direct effects, an important indirect role of the organism factor is  
284 apparent in atmospheric N inputs. Nitrogen inputs rates via dry deposition and cloudwater are  
285 affected by community composition and forest structure (Lovett, 1994). Conifers generally  
286 show higher N throughfall fluxes than broadleaf vegetation, reflecting greater surface area and  
287 surface roughness that facilitates higher rates of dry-deposition scavenging from the air (Lovett,  
288 1994). An extensive study in Europe reported N throughfall fluxes under conifer canopies that  
289 exceeded bulk N deposition rates by a factor of ~4 (Kristensen et al., 2004). Another major  
290 influence of the organism-factor on local N deposition inputs is seen in comparisons of forest  
291 gaps and canopy edges. (Lindberg and Owens, 1992) reported much higher nitrate throughfall  
292 fluxes in mature spruce forest edges than in localized gaps and forest interiors. They attributed  
293 this difference to localized controls on dry N deposition rates, which are affected by forest  
294 structure, aspect and exposure in highly fragmented ecosystems.

295 Beyond the atmosphere, geobiological controls in the organism factor are widely known  
296 to influence the physical and chemical weathering of rock-derived elements. This occurs though  
297 direct and indirect mechanisms mediated by plant-microbe interactions. “Rock-eating-fungi”  
298 have been shown to directly accelerate the weathering of calcium ( $\text{Ca}^{2+}$ )- and potassium ( $\text{K}^+$ )-

299 bearing lithologies in forests (Jongmans et al., 1997; van Scholl et al., 2008). Past work points to  
300 mycorrhizal fungi (i.e., root symbionts) in the weathering of feldspar minerals via the  
301 production of various organic acids and chelates, such as succinate, citrate, oxalate, formate  
302 and malate, which chemically deplete rock minerals actively (Jongmans et al., 1997; Hoffland et  
303 al., 2004; van Scholl et al., 2006; van Scholl et al., 2008). Other mechanisms include the  
304 production of siderophores, particularly via ectomycorrhizae (ECM), which bind iron and  
305 thereby accelerate soil mineral weathering and horizon development (Taylor et al., 2009).  
306 Indirectly, plant investment in belowground root and hyphal networks increase reactive mineral  
307 surfaces, provide C for microbial decomposition, and contribute to increased soil acidity.  
308 Together, these factors are thought to enhance chemical weathering rates by a factor of 2 – 10  
309 (Drever, 1994; Andrews and Schlesinger, 2001). Such vegetation-driven weathering rates in  
310 upland ecosystems have been suggested to vary with atmospheric CO<sub>2</sub> concentrations over the  
311 past 24 million years (Pagani et al., 2009).

312           Although less is known about direct geobiological controls on soil N weathering  
313 reactions, isotopic evidence suggests that N can be directly transferred from rocks to plants in  
314 ecosystems, which might be mediated by fungal mutualism (Fig. 2). The isotopic composition  
315 ( $\delta^{15}\text{N}$ ) of rock N sources (green line) can be exceedingly enriched compared to atmospheric N  
316 inputs (Holloway and Dahlgren, 2002; Houlton and Bai, 2009), which are typically between 0 to  
317 -3 per mil (dashed line). Across a set of temperate forest sites dominated by Douglas fir, the  
318  $\delta^{15}\text{N}$  of foliage converges on that of rock  $\delta^{15}\text{N}$  when rock concentrations exceed ~500 ppm N;  
319 yet soil  $\delta^{15}\text{N}$  is consistently higher than rocks and other N input pathways as the result of  
320 fractionating losses of N (Martinelli et al., 1999; Amundson et al., 2003; Houlton et al., 2006;

321 Houlton and Bai, 2009). This suggests active uptake of rock N by plants in N-rich parent  
322 material, which is likely to be facilitated by root-associated ECM in Douglas fir forests.  
323 Examining this hypothesis in a range of sites by measuring mycorrhizal abundance, N  
324 concentrations and  $\delta^{15}\text{N}$  of various N pools is deserving of future work.

325

### 326 **2.3 Topography**

327 Topographic gradients regulate erosion and chemical weathering rates; thus, this factor  
328 affects N fixation (discussed in Parent Material below) and could strongly affect rock N inputs to  
329 soil. At large scales, erosion rates are strongly correlated with topographic relief (Montgomery  
330 and Brandon 1994, Portenga and Bierman 2011), and global biogeochemical analysis points to  
331 widespread control of tectonics, uplift and orogeny on the removal of elements from the land  
332 (Stallard and Edmond, 1983; Raymo et al., 1988; Milliman and Syvitski, 1992; Stallard, 1998).  
333 Under the steady-state, relief is treated as the balance between uplift and erosion, with active  
334 orogens representing potential “hot-spots” of rock-derived element availability in the soil. At  
335 landscape scales, denudation (combined physical erosion plus chemical weathering) increases  
336 with local relief exponentially (Montgomery and Brandon, 2002; Portenga and Bierman, 2011).  
337 Both empirical data and theoretical models show that chemical weathering is maximized in  
338 landscapes with moderate to high erosion owing to the rapid exhumation of fresh reactive  
339 minerals (Stallard and Edmond, 1983; Riebe et al., 2004; West et al., 2005; Gabet and Mudd,  
340 2009). At very high erosion rates, however, chemical-weathering rates may decline due to  
341 thinning of the regolith and soils, effectively reducing the amount of reactive surface area  
342 available for chemical weathering.



343           Among landscapes with high relief, soil nutrient availability reflects a dynamic tension  
344 between chemical weathering and erosion. Work by Porder et al. (2007) suggested that rock-  
345 derived nutrient availability ought to peak at moderate uplift rates where the ratio of  
346 weathering inputs/losses reaches a global maximum. Within stable landforms, low  
347 denudation rates greatly reduce element inputs via rocks; in contrast, high relief environments  
348 often display high chemical weathering rates but large element losses to erosion and mass  
349 wasting, which limits the accumulation of soil available nutrients. Model-based abstractions of  
350 these geomorphic principles suggest that lowland tropical sites in stable landforms are likely to  
351 be P-limited, whereas areas of moderate relief and high chemical weathering are less likely to  
352 be limited by P (Porder et al., 2007; Porder and Hilley, 2011). Similarly, rock N inputs in low-  
353 relief landscapes are expected to be substantially lower than moderate-to-high relief  
354 environments owing primarily to low rates of rock exhumation and denudation. The  
355 development of thick zones of saprolite/regolith weathering in some low-relief landscapes may  
356 also result in rock N weathering at depth within the critical zone, beyond the reach of plant life.

357           At local scales, erosion and soil production (conversion of rock to soil) is proportional to  
358 slope and is linearly correlated with the negative curvature of topography (Heimsath et al.  
359 1997, Roering et al. 1999). Both weathering rates and erosion in hillslope sequences are  
360 generally highest at convex positions near ridgetops (i.e. shoulder positions), contributing to  
361 accumulation of weathering products in concave positions lower in the landscape (i.e.  
362 footslopes and toeslopes; Milne, 1936; Gessler et al., 2000; Yoo et al., 2007). Consequently, the  
363 highest rates of weathering become spatially decoupled from where nutrient accumulation  
364 (and putatively plant nutrient availability) is greatest (Yoo et al., 2006; Yoo et al., 2007).

365 Weathering rates at hillslope summit positions are variable and slope dependent, but when  
366 these positions are flat and non-eroding (i.e. stable geomorphic surfaces), weathering rates are  
367 generally lowest. These conditions can promote long-term declines in soil fertility and  
368 functioning over millennia, perhaps best demonstrated in highly weathered stable-surfaces  
369 where the stunted Pygmy forest occurs in Mendocino, California (Jenny et al., 1969; Izquierdo  
370 et al., 2013). Landslides can remove soil that is highly weathered and provide biological access  
371 to un-weathered parent material; this mechanism has been demonstrated to rejuvenate  
372 elements such as P in otherwise P-limited volcanic soils in Hawaii (Vitousek et al., 2003; Porder  
373 et al., 2005).

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

381         For example, upslope (high elevation) sites exhibited substantially higher net N  
382 mineralization and nitrification rates, larger soil inorganic N pools, and elevated foliar  $^{15}\text{N}/^{14}\text{N}$   
383 compared to low elevation sites developing on sedimentary (and putatively N-rich, Holloway et  
384 al., 1998; Holloway and Dahlgren, 2002) parent material in the Great Smokey Mountains  
385 (Garten and Vanmiegroet, 1994). Likewise, total soil N concentrations were elevated in  
386 shoulder positions of cantenae underlain by N-rich shale substrates in the Shinga prefecture,

387 Japan (Hirobe et al., 1998). More directly, Morford et al. (2011) demonstrated that the N  
388 content of soils and forest foliage collected from erosional slopes of N-rich metasedimentary  
389 rocks (350–950 ppm) was elevated by more than 50% compared with similar temperate forest  
390 sites underlain by N-poor igneous parent material (30–70 ppm). For N-bearing lithologies, this  
391 means that rock N inputs could offset local N losses from erosional hillslope positions while also  
392 contributing to higher total N inputs at landscape scales, thus altering topography-driven  
393 patterns of N availability that are closer to expectations for other rock-derived elements  
394 (Morford, 2014).

395

#### 396 **1.4 Parent Material**

397 We suggest that the parent material factor regulates patterns and rates of N fixation  
398 and rock input pathways. Rocks contain ~99% of Earth's fixed N (Schlesinger, 1997), even when  
399 excluding mantle reservoirs that interact sparingly with earth surface processes (Bebout et al.,  
400 2013). Approximately 75% of the fixed N reservoir within the continental crust is found in  
401 sedimentary and meta-sedimentary rocks (Goldblatt et al., 2009), primarily reflects higher rates  
402 of N fixation compared to denitrification to N<sub>2</sub> gas over Earth history. Nitrogen concentrations  
403 are much higher in sedimentary/meta-sedimentary than igneous parent materials, though  
404 either class can contain appreciable geological N (Holloway and Dahlgren, 2002). Further,  
405 reservoirs of geological N can occur as silicate-bound NH<sub>4</sub><sup>+</sup>, organic-N in sedimentary organic  
406 matter, or nitrate in evaporites. Variation in both the amount and form of rock N is controlled  
407 by local depositional environments, the degree of biological and thermal diagenesis in  
408 sedimentary basis, and the degree of N volatilization during metamorphism (Bebout and Fogel,

409 1992; Hedges and Keil, 1995; Hedges et al., 1999; Boudou et al., 2008). Rock-bound nitrate can  
410 be seen in desert/arid ecosystems where hydrological losses are minimal and nitrate  
411 accumulates at depth or in the surface of caliche deposits (Walvoord et al., 2003). On average,  
412 Holloway and Dahlgren (2002) found that the parent material factor is a strong driver of rock N  
413 contents, with trace amounts of N found in cratonic assemblages to >20,000 ppm N in  
414 sedimentary rocks such as coal. Generally, N enrichment is highest among fine-grained  
415 siliciclastic rocks (i.e. shales, mudstones), and their low-grade metamorphic counterparts (i.e.  
416 slate, phyllite, and mica-schist). These rocks comprise ~30% of earth's continental surfaces and  
417 have an average N concentration equal to 700 – 1000 mg N kg<sup>-1</sup> (Durr et al., 2005; Goldblatt et  
418 al., 2009; Morford, 2014).

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

430 concentrations across a sequence of sites in Sweden; they attributed variations in soil N to  
431 variations in N parent material chemistry.

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

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

451 influenced soil P availability and thus the response of free-living fixation to P vs. Mo  
452 (Wurzburger et al., 2012).

453

#### 454 **1.5 Time**

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

469 Evidence from a variety of ecosystems generally supports the expectation for a decrease  
470 in N fixation over primary succession (Walker, 1993). In both newly formed volcanic (Vitousek,  
471 2004) and de-glaciated sediments (Chapin et al., 1994) cyanolichens are among the earliest  
472 colonizers, with direct and indirect evidence for significant free-living N fixation rates in fresh

473 parent material (Schlesinger et al., 1998; Crews et al., 2001). These pioneering species provide  
474 N to facilitate more diverse ecosystem communities as succession proceeds, but are ultimately  
475 excluded owing to light limitations and life-history factors as forest canopies develop further  
476 (Chapin et al., 1994; Chapin et al., 2002; Vitousek et al., 2002; Walker et al., 2003). Work along  
477 recently deglaciated environments shows that populations of symbiotic fixers have an  
478 advantage in early primary succession. Once N pools reach a critical threshold, however,  
479 competition favors non-fixing species such as black spruce, which can acquire N from the soil at  
480 minimal cost compared to fixation and can outcompete alder for light (Chapin et al., 1994). A  
481 similar pattern was found in different New Zealand sites, wherein early colonizing plants with  
482 the capacity to fix N were replaced by non-fixing species over the course of primary succession  
483 (Walker et al., 2003).

484         This pattern is not always observed, however, particularly as fine-scale soil  
485 heterogeneity alters local nutrient availability and decouples of free-living fixers from average  
486 soil conditions (Reed et al., 2011). For example, Menge and Hedin (2009) showed that symbiotic  
487 N fixation via *Coriaria arborea* averages ~11 Kg N/ha/yr until >60 years of pedogenesis.  
488 Thereafter, this species was competitively excluded from older sites along the Franz Josef  
489 chronosequence in New Zealand owing to a host of life-history and ecosystem constraints. In  
490 contrast, free-living N fixation in various soil pools and the canopy were variable yet persistent  
491 during primary succession, consistent with studies of free-living paths along the Hawaii  
492 chronosequence (Matzek and Vitousek, 2003). And, work on free-living fixation in the boreal  
493 suggests a pattern that opposes Jenny's (1958) model: rates of N fixation in feather moss

494 communities have been shown to increase over primary succession, likely in response to  
495 declines in N availability over time (Zackrisson et al., 2004).

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

506           In contrast to fixation, direct knowledge of rock N inputs during primary succession is  
507 sparse. Most studies assume that rock N inputs are uniformly unimportant in newly formed  
508 ecosystems (*sensu* Walker and Syers, 1976), rather than measuring and examining the potential  
509 for rock weathering to alter N inputs over succession. This assumption is probably true for  
510 igneous substrates (e.g., Hawaii chronosequence, Vitousek, 2004) where parent material N  
511 contents are typically low (Dahlgren and Holloway, 2002); but not for many sedimentary and  
512 meta-sedimentary substrates (see also Parent Material above).

513           Binkley et al. (2000) analyzed evidence for surprisingly high rates of N accumulation in  
514 terrestrial ecosystems as based on knowledge of atmospheric N input pathways. Their  
515 assessment placed high confidence in the unexplainably high N accumulation (soil plus



516 vegetation) rates observed for forests in Walker Branch, Tennessee (>43 to 70 kg N/ha/yr,  
517 (Johnson and Todd, 1998) where the lithology is dominated by differential sequences of marine  
518 carbonate and siliciclastic sediments. In fact, a closer inspection of N accretion studies (Binkley  
519 et al., 2000; Johnson and Turner, 2014) reveals that eight of the ten temperate sites with  
520 unusually high N accumulation rates (i.e., > 20 kg ha yr<sup>-1</sup>) were from sites with high geologic N  
521 input capacities (see supplemental Table; Fig. 5). The remaining two sites were from the  
522 Hubbard Brook Sandbox experiment (Bormann et al, 1993) and the Mt. Shasta mudflow  
523 chronosequence (Dickson and Crocker, 1953) where rock N inputs are unlikely. While a number  
524 of the sedimentary sites also showed low (or negative) N accretion rates, there does not appear  
525 to be divergent pattern between putatively N-rich vs. N-poor geologic-substrates; yet, nearly all  
526 the sites reporting high N accumulation rates come from sites on sedimentary parent materials  
527 (Fig. 5). This data reanalysis provides testable evidence for rock N sources in the “missing N  
528 inputs” across a range of temperate forest sites.

529

## 530 **2.6 Anthropogenic**

531 Humans have become the single-greatest force in terrestrial N inputs. Agricultural  
532 expansion, synthetic fertilizer production, and fossil fuel combustion have doubled the amount  
533 of reactive N circulating in the terrestrial biosphere (Delwiche, 1970; Vitousek et al., 1997;  
534 Galloway and Cowling, 2002; Fowler et al., 2013). The anthropogenic factor plays a major role  
535 in atmospheric N deposition inputs into natural soil systems, whereas rock mining activities  
536 have mobilized geological N but not in a way that has greatly changed N inputs to natural sites.  
537 Further, human alternations can be classified as intentional or unintentional (Houlton et al.,

538 2013), with the former arising via fertilizer inputs and domestication of legumes, and the latter  
539 as fixed N derived from fossil fuel combustion and air-borne agricultural losses of N. From a  
540 global budget perspective, agricultural emissions of NO<sub>x</sub> and NH<sub>3</sub> comprise a large-scale  
541 recycling term, despite representing a new N input to downwind ecosystems.

542         Hence, the anthropogenic factor has most clearly altered patterns of N deposition  
543 inputs into natural or unmanaged soil systems worldwide (Holland et al., 1997; Lamarque et al.,  
544 2005). Prior to widespread human activities, a small amount (~5 to 10 Tg N/yr) of N was fixed  
545 during lightening strikes and washed out of the atmosphere. The airborne sources of N through  
546 human activities have greatly changed patterns of N deposition inputs from the pre-industrial  
547 state, such that N deposition maps well with areas of fertilizer use and industrialization (Fig. 6).  
548 Current estimates suggest that ~30% of anthropogenic N deposition is derived from fertilizers,  
549 with the majority (i.e., 70%) derived from mobile and stationary fossil fuel sources (Schlesinger,  
550 2009). Whereas the largest post-industrial growth in anthropogenic N deposition has occurred  
551 at higher latitudes (Galloway et al., 2004), N deposition inputs to soils and ecosystems are  
552 expected to expand to tropical and sub-tropical environments as developing economies grow  
553 this century (Matson et al., 1999; Lamarque et al., 2005), as is already clear throughout much of  
554 China (Liu et al., 2013). The implications of anthropogenic N deposition are far-reaching and  
555 widespread and underlie a host of land, air and water quality issues (Vitousek et al., 1997;  
556 Houlton et al., 2013).

557

### 558 **3. Discussion and Implications**

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

568           First, N limitation to terrestrial plant productivity and microbial functioning is  
569 widespread (Vitousek and Howarth, 1991; LeBauer and Treseder, 2008); yet questions remain  
570 over the reasons for this biogeochemical phenomenon. Whether N limitation is transient or  
571 sustained is largely determined by the magnitude of N inputs, their spatial variation, and how N  
572 inputs are balanced by N losses to erosion, the hydrosphere and the atmosphere (Hedin et al.,  
573 1995; Vitousek et al., 2002; Houlton et al., 2003; Houlton and Bai, 2009; Cleveland et al., 2013).  
574 The new synthesis that considers both rock and atmospheric N sources, and how such sources  
575 are regulated by state-factors and biogeochemical processes, will improve our understanding of  
576 N limitation to plant productivity and soil microbial processes across Earth's diverse terrestrial  
577 ecosystems. For example, application of state-factor principles has lead to a richer  
578 understanding of patterns of P limitation patterns even in the absence of direct empirical  
579 experiments (Porder and Hilley, 2011). Fertilization experiments are laborious and difficult to  
580 implement in many natural ecosystems (Sullivan et al., 2014a), and do not reveal controls on

581 nutrient limitation patterns. Knowledge of how state-factors are likely to shape the sources of N  
582 that dominate among different biogeochemical environments will improve our understanding  
583 of the causes and consequences of terrestrial N limitation.

584         Second, explicit consideration of rock and atmospheric N sources will improve our  
585 understanding of terrestrial ecosystem feedbacks on climate change. Global biogeochemical  
586 projections that consider N availability point to much less CO<sub>2</sub> capture and soil C sequestration  
587 than those without an N cycle (Hungate et al., 2003; Thornton et al., 2007; Wang and Houlton,  
588 2009; Zaehle et al., 2010a). The recent IPCC AR5 report included only one N cycle model that,  
589 when coupled to two different Earth System Models (ESMs), suggested less CO<sub>2</sub> uptake and  
590 more climate warming than model simulations in the absence of N limitation (Ciais, 2013). The  
591 uncertainty in terrestrial N input paths and C by N interactions could result in up to 2 degrees  
592 Celsius of additional warming by 2100 (Wang and Houlton, 2009). However, none of these  
593 models have considered N inputs via rock sources, and the potential for this N input path to  
594 alter patterns of ecosystem N and C storage (e.g., Morford et al., 2011). The new synthesis  
595 argues for important controls over rock N inputs in all but one (i.e., anthropogenic) state factor,  
596 and articulates controls that can be used to inform models that consider all three N input  
597 pathways together. All N input paths can display climate-dependencies, but most clearly in the  
598 case of rock N weathering and biological N fixation inputs.

599         Third, conceptual models based on the new synthesis will advance our understanding of  
600 variation in soil N fertility and update nutrient cycling concepts (Fig. 7). Pedogenic models have  
601 assumed that fixation and deposition can alter patterns of ecosystem development but have  
602 hitherto neglected rock N sources (Walker and Syers, 1976). By separating the parent material

603 factor between N-poor vs. N-rich substrates, we propose different trajectories for ecosystem N  
604 availability as a function of parent material, organisms, time and topographic relief. Factors that  
605 allow for high rock N inputs – N-rich sedimentary rocks, early succession, moderate relief –  
606 would be expected to deviate from the standard model of N limitation, whereas N-poor  
607 lithologies would be expected to follow previously articulated patterns of nutrient limitation  
608 during ecosystem pedogenesis and landform development, with N fixers playing a more active  
609 role in early succession (Fig. 7). We recommend experiments that superimpose state factors in  
610 natural site arrays (e.g., as done in Hawaii sensu Vitousek, 2004) to systematically isolate  
611 controls on N weathering inputs and examine its role in primary succession and landscape  
612 patterns of N fertility.

613         Although we have largely examined N inputs within individual state-factors, N source  
614 pathways are likely to affect one another within a given state-factor setting. For example,  
615 theory and experimental research demonstrates that external N inputs reduce the capacity for  
616 terrestrial N fixation (Vitousek et al., 2002; Reed et al., 2011; Fig. 3). This dynamic occurs as the  
617 competitive balance shifts in favor of N uptake from the soil, which can occur at a minimal cost  
618 compared to N fixation under increasing N concentrations (Vitousek and Field 1999; Rastetter  
619 et al. 2001; Houlton et al. 2008). This means that state-factors favoring high N inputs via  
620 deposition and rock weathering inputs with high N/P could reduce rates of fixation in a given  
621 soil system, all else remaining equal. Alternatively, given plant-litter controls on free-living N  
622 fixation rates (Vitousek and Hobbie, 2000), it is possible for fixation along free-living paths to  
623 increase in high rock N input sites. If plant litter quality increases in response to high rock N  
624 inputs, free-living rates of N fixation could increase rather than decrease.

625           Indeed, that biological N fixation can respond rapidly to changes to N input pathways is  
626 what marks N as fundamentally different from all other major soil nutrients (Vitousek et al.,  
627 2010). Phosphorus, cations and essential trace metals exhibit both rock and atmospheric input  
628 paths that are clearly controlled by state factors; yet they lack important gaseous phases and an  
629 N fixation analogue to promote rapid feedback among atmospheric and rock sources. We  
630 conclude that ecosystem analysis of N inputs must consider how factors altering the pattern  
631 and magnitude of N weathering and deposition can influence fixation, in contrast to state-  
632 factor controls on other soil elements in which input-sources are not directly tied to one  
633 another.

634           The state-factor approach we adopt provides testable predictions for the new synthesis,  
635 but it by no means should be taken as the only approach to understanding atmosphere,  
636 biosphere and geosphere effects on the N cycle. We view the state-factor model as a powerful  
637 and proven integrative tool that offers useful sets of concepts to help guide experimental  
638 research in the Earth system sciences. It is historically important to soil and ecosystem science,  
639 and in the case of N, places this element in a similar construct with the classic rock derived  
640 elements. The weakness of the state-factor approach lies in the lack of quantitative predictions  
641 of N input kinetics and the absence of focus on individual processes. We suggest that process  
642 based model development should go hand-in-hand with state factor approaches to  
643 understanding the new synthesis. This approach has proven quite effective for understanding  
644 weathering of the classic rock derived elements. For example, work along a set of  
645 chronosequences has been used to develop process-based models and quantitative predictions  
646 of P inputs and limitation patterns globally (Porder and Hilley, 2011). We envision parallel

647 activities, in which state factor assessments are combined with an examination of reaction  
648 kinetics, particularly N fixation and N weathering kinetics in controlled settings, can give rise to  
649 a more general understanding of N inputs and individual process-based modeling of the  
650 terrestrial N cycle. Experiments designed to evaluate the kinetics of chemical weathering vs.  
651 physical erosion will be vital to determining the availability of rock N sources to terrestrial biota.

652         Finally, the new synthesis we propose has implications for many different aspects of  
653 global environmental change. As humanity's imprint on the Earth system expands and  
654 intensifies, understanding the global consequences of reactive N inputs to natural soil systems  
655 will become increasingly important. On the one hand, the N saturation hypothesis argues for  
656 declines in plant productivity and terrestrial C storage as chronic increases in anthropogenic N  
657 deposition inputs acidify soils, cause nutrient imbalances, and mobilize soil  $Al^{3+}$  forms to toxic  
658 thresholds (Aber et al., 1989). However, patterns of N saturation have been difficult to  
659 understand, and could be affected by the amount of rock N weathering inputs in different  
660 ecosystems (Dahlgren, 1994). In contrast, the progressive N limitation hypothesis recognizes  
661 the role of rising levels of  $CO_2$  in stimulating plant photosynthesis and productivity, and instead  
662 argues for enhanced N limitation and growth of soil and ecosystem N sinks (Luo et al., 2004).  
663 Research on progressive N limitation has been mixed, and could also be affected by all three N  
664 input pathways, with evidence for rock N inputs substantially altering the C sink capacity of  
665 forest ecosystems (Morford et al., 2011). A greater appreciation of the pattern, magnitude and  
666 response of atmospheric vs. rock N inputs will go a long way toward understanding changes to  
667 Earth's diverse soils, landscapes and ecosystems in the Anthropocene.

668

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

State Factor	Biological N <sub>2</sub> Fixation	N Deposition	N Chemical Weathering
<b>Climate</b>	Generally increase with temperature; global optimum ~25 degrees Celsius	---	Increase with precipitation and to lesser degree with temperature
<b>Organism</b>	Presence of fixers increases rate	Local effect; higher in conifers than deciduous vegetation	Increase with productivity and presence of fungal mutualism, geobiological control
<b>Parent Material</b>	Higher in P and micro-nutrient rich substrates	---	Higher in N-rich sedimentary than N-poor igneous substrates
<b>Relief</b>	Highest at intermediate relief	Higher at high elevation sites	Highest at intermediate relief
<b>Time</b>	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
<b>Anthropogenic</b>	---	Increase with fossil fuel combustion and synthetic N fertilizer sources	---

## List of Figures

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.  $\delta^{15}\text{N}$  of live foliage, soil and parent material (rock) vs. rock N concentrations across Douglas fir forest. The dashed line reflects that  $\delta^{15}\text{N}$  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/yr). 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/yr. (modified by Galloway et al., 2008).

Figure 7. Conceptual diagram of interacting state-factor controls (organism, parent material, topography, time) on terrestrial N inputs. 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 comprises a small fraction of the long-term N input.

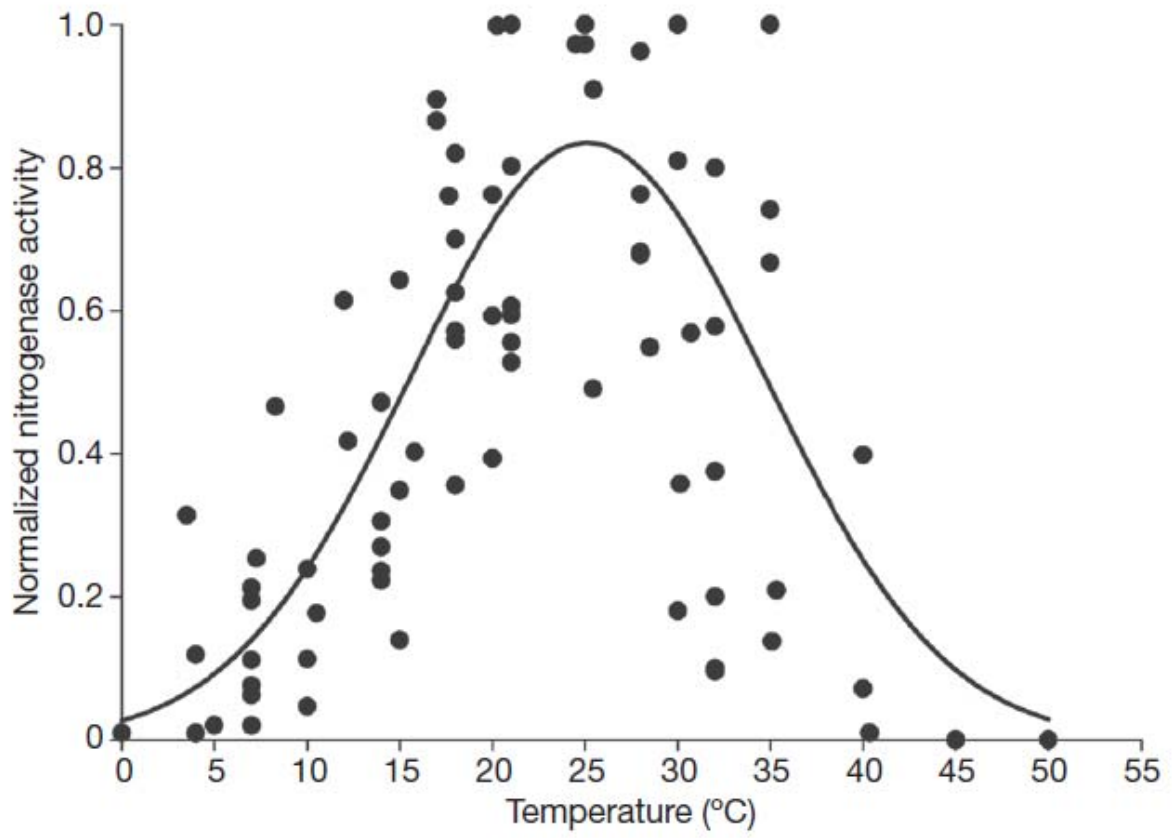


Figure 1

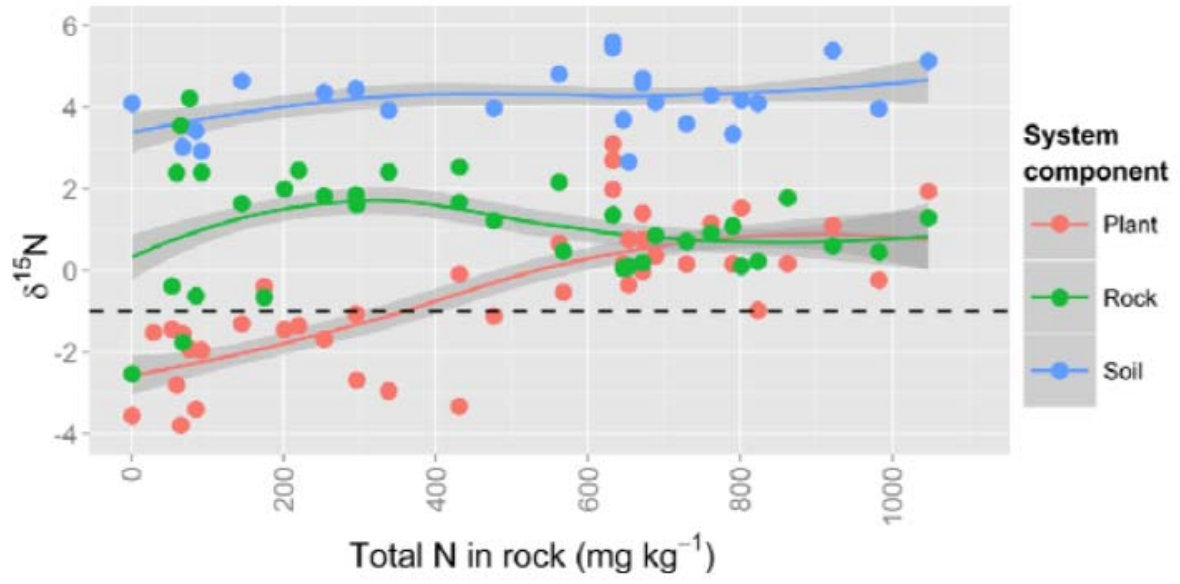


Figure 2

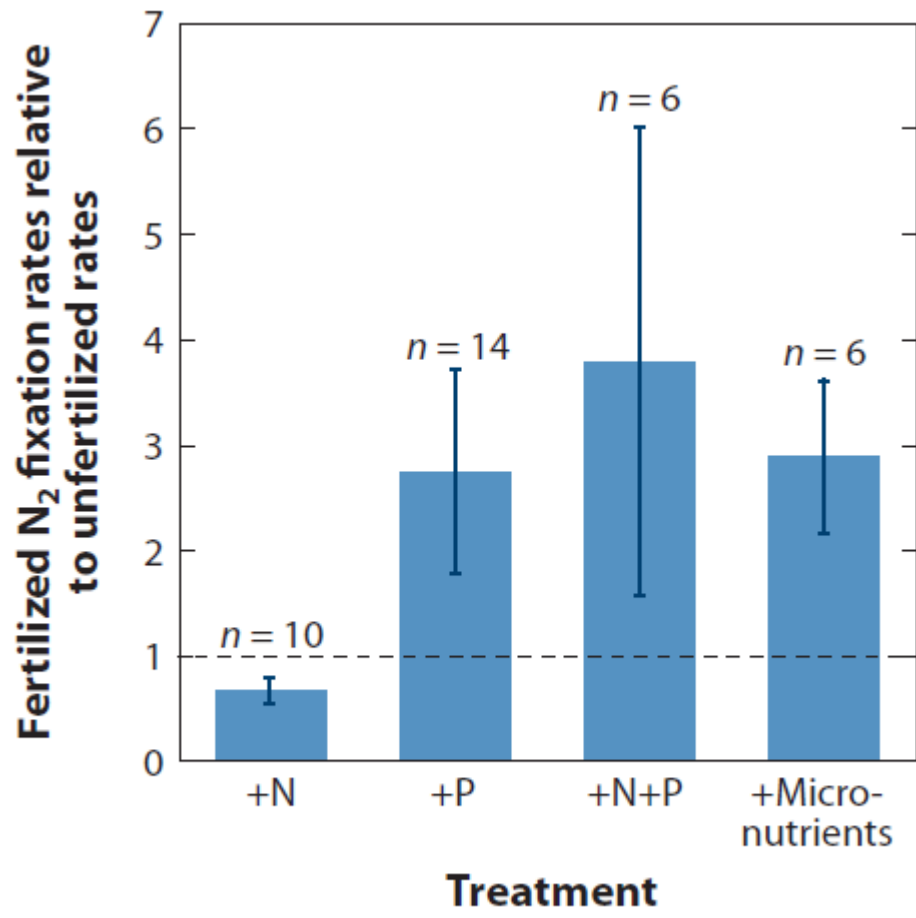


Figure 3

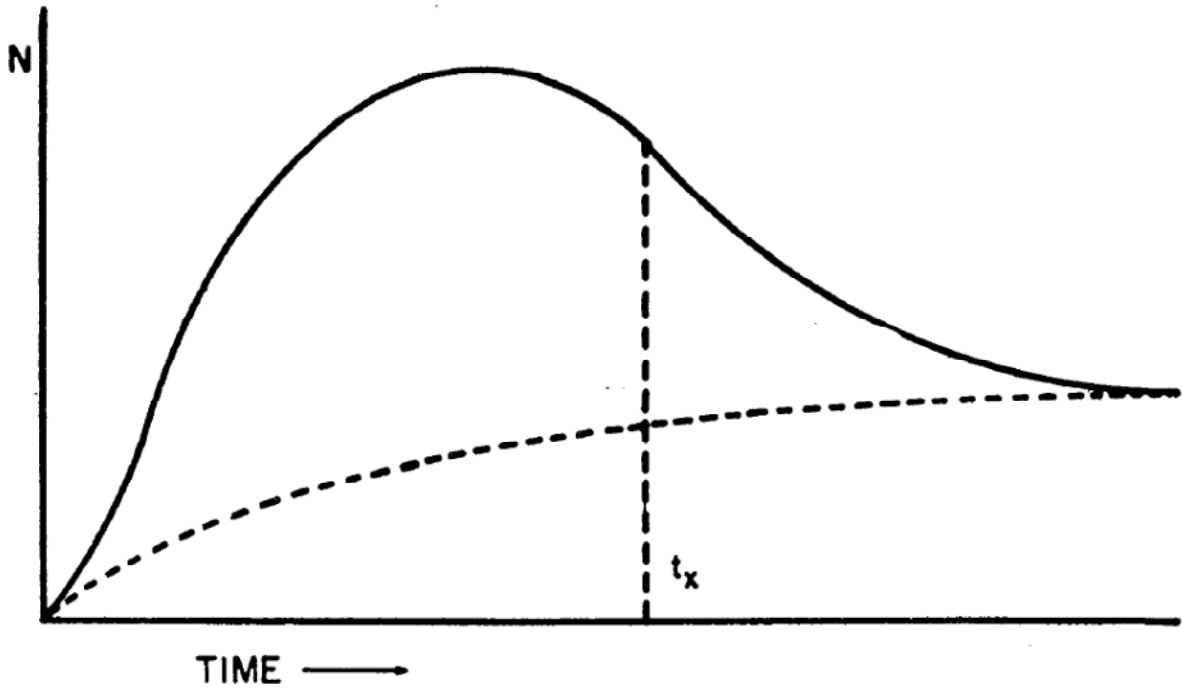


Figure 4

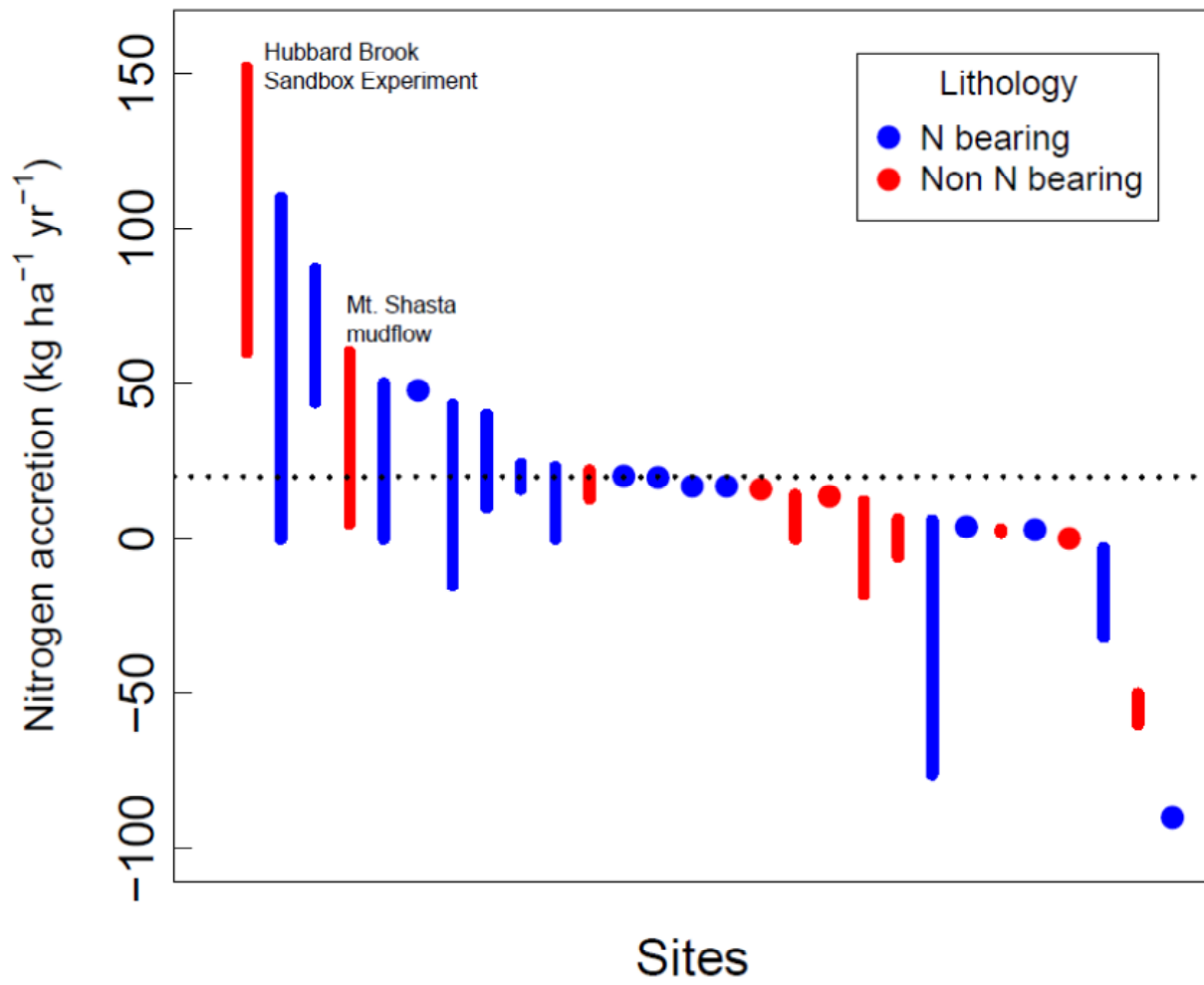


Figure 5



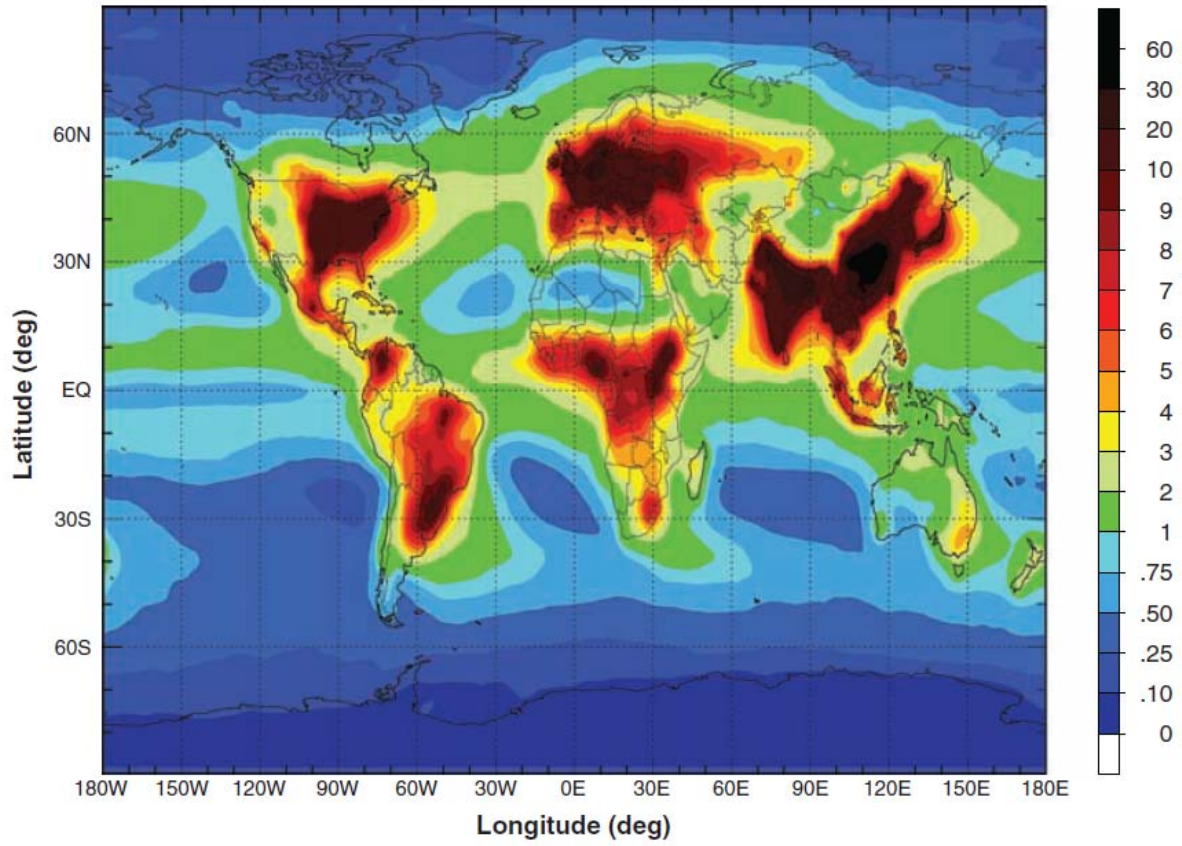


Figure 6

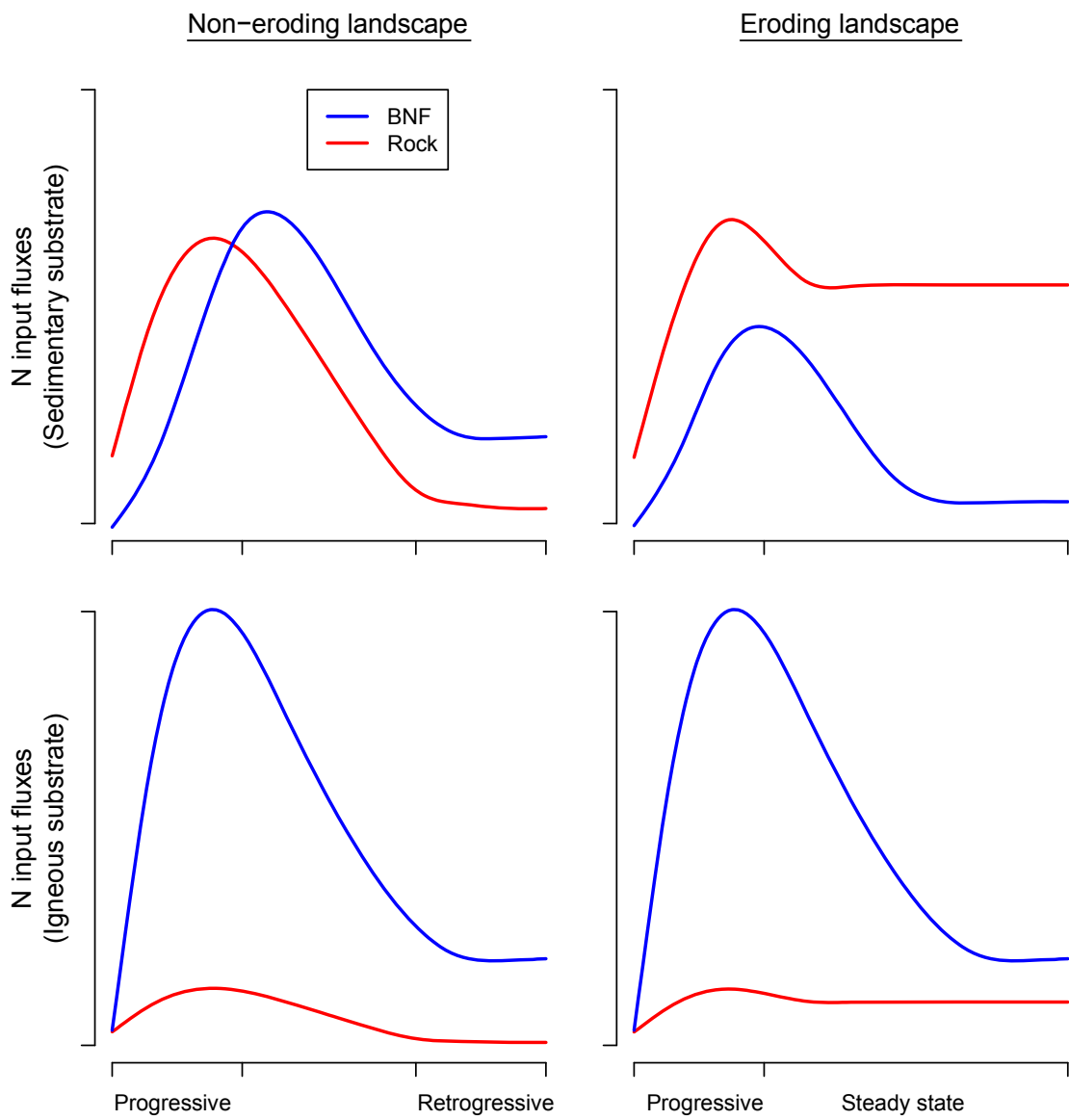


Figure 7