

TERRESTRIAL PHOSPHORUS LIMITATION: MECHANISMS, IMPLICATIONS,  
AND NITROGEN-PHOSPHORUS INTERACTIONS

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1 ABSTRACT

2 Nutrient limitation to primary productivity and other biological processes is widespread  
3 in terrestrial ecosystems, and nitrogen (N) and phosphorus (P) are the most common limiting  
4 elements, both individually and in combination. Mechanisms that drive P limitation – and their  
5 interactions with the N cycle – have received less attention than mechanisms causing N  
6 limitation. We identify and discuss 6 mechanisms that could drive P limitation in terrestrial  
7 ecosystems. The best-known of these is depletion-driven limitation, in which accumulated P  
8 losses during long-term soil and ecosystem development contribute to what Walker and Syers  
9 (1976) termed a “terminal steady state” of profound P depletion and limitation. The other  
10 mechanisms are soil barriers that prevent access to P; transactional limitation, in which  
11 weathering of P-containing minerals does not keep pace with the supply of other resources; low-  
12 P parent materials; P sinks; and anthropogenic changes that increase the supply of other  
13 resources (often N) relative to P. We distinguish proximate nutrient limitation (which occurs  
14 where additions of a nutrient stimulate biological processes, especially productivity) from  
15 ultimate nutrient limitation (where additions of a nutrient can transform ecosystems). Of the  
16 mechanisms that drive P limitation, we suggest that depletion, soil barriers, and low P parent  
17 material often cause ultimate limitation because they control the ecosystem mass balance of P.  
18 Similarly, demand-independent losses and constraints to N fixation can control the ecosystem-  
19 level mass balance of N and cause it to be an ultimate limiting nutrient.

20 Key Words: Biogeochemistry, Chronosequence, Nitrogen, Nutrient Limitation, Phosphorus,  
21 Proximate versus Ultimate

22

## INTRODUCTION

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The importance of phosphorus (P) and nitrogen (N) limitation to primary production and other ecosystem processes has been demonstrated in a wide variety of terrestrial ecosystems. Much of the conceptual framework for terrestrial nutrient limitation was synthesized by Walker and Syers (1976), who suggested that because P is derived primarily from rock weathering, ecosystems begin their existence with a fixed complement of P from which even very small losses can not readily be replenished. Consequently, ecosystems with very old soils can become depleted in P. Walker and Syers measured total soil P and some of its chemical forms in a number of New Zealand chronosequences (substrate age gradients), and demonstrated a pattern of lower total P and an increased fraction of recalcitrant P in older substrates; they suggested these old sites represent a “terminal steady state” of P depletion and biological limitation.

In contrast, combined N is nearly absent from most igneous and metamorphic rocks; outside of ecosystems underlain by certain sedimentary and meta-sedimentary rocks (Dahlgren 1994; Holloway et al. 1998), most terrestrial ecosystems are largely devoid of N as they begin their development (Walker and Syers 1976). Unlike P, N is accumulated from the atmosphere – rapidly via biological N fixation, where symbiotic N fixers dominate an early stage of ecosystem development, or more slowly via atmospheric deposition and dispersed sources of biological fixation. Accordingly, biological processes in many ecosystems on young soils may be limited by low supplies of N.

This temporal pattern in P versus N limitation gives rise to a geographical one (Vitousek and Sanford 1986), because over the last several million years high latitude systems have been systematically and cyclically influenced by glaciation and related processes (such as loess deposition) that rejuvenate their supply of P and other rock-derived nutrients and can remove

45 their stocks of N. In contrast, no glaciers have existed in the lowland tropics for hundreds of  
46 millions of years – and so a larger fraction of tropical sites could approach Walker and Syers’  
47 terminal steady state of P depletion and limitation.

48 While developmental and latitudinal gradients in N versus P limitation are supported by  
49 many observations (below) and make sense logically, a number of studies have reported patterns  
50 of P and N limitation that differ from these expectations, suggesting that additional or alternative  
51 mechanisms could underlie P limitation. Wardle et al (2004) evaluated 6 well-studied  
52 chronosequences that ranged from ~20° to ~65° in latitude, in which the oldest sites were lower  
53 in biomass and/or productivity than intermediate-aged sites. Wardle et al. (2004) concluded that  
54 this decrease was associated with a lower availability of P relative to N, in comparison with  
55 younger sites on each sequence – although evidence that changes in P caused changes in  
56 biomass/productivity was sparse for several sequences. Because of glacial processes, the oldest  
57 sites in their two high-latitude chronosequences originated in the Holocene (<15 ky), making  
58 them younger than the fertile "intermediate" aged sites in their two tropical / subtropical  
59 sequences, in which the oldest, P-poor sites are 600 and 4,100 ky. It seems unlikely that  
60 ecosystem development proceeds to P depletion orders of magnitude more rapidly in boreal than  
61 in tropical environments; more likely the low P status of the older high-latitude sites is driven by  
62 different processes than in the tropical sites.

63 Evidence for widespread P limitation in terrestrial ecosystems outside the tropics has not  
64 been drawn solely from chronosequences. For example, Wassen et al. (2005) evaluated the  
65 distribution of endangered plants in putatively N- versus P-limited sites across a long Eurasian  
66 transect, and concluded that many are confined to sites where foliar analyses suggest that the  
67 main limiting nutrient is P, not N. More directly, a recent meta-analysis by Elser et al. (2007)

68 summarized patterns of N versus P limitation from fertilization experiments conducted in 1079  
69 sites in marine (243 sites), freshwater (653), and terrestrial (173) ecosystems. Contrary to  
70 expectations that N supply typically limits plant growth in temperate forests, grasslands and the  
71 coastal ocean while P limits freshwater ecosystems and tropical forests (Schindler 1977,  
72 Vitousek and Howarth 1991, Howarth and Marino 2006), they found the mean effect of P (when  
73 added alone) to be substantial – similar to that of N added alone - across terrestrial ecosystems.  
74 Mean responses to N plus P additions were even greater. Further, they found little evidence for  
75 latitudinal or growth-form (eg grassland, shrubland, forest) differences in the mean  
76 responsiveness of plant growth to N versus P, although the few tropical forest experiments they  
77 summarized reported more limitation by P than by N. Another recent meta-analysis (LeBauer  
78 and Treseder 2008) focused on N in terrestrial ecosystems; they too found no significant  
79 relationship between the extent of N limitation and latitude, when similar sites were compared.  
80 Elser et al. (2007) concluded that many ecosystems are poised near the point where N and P are  
81 equally limiting to the growth of plants. Consequently, they suggested that the identity of  
82 limiting nutrients in terrestrial environments should not be assumed, and that both science and  
83 management should recognize that ongoing human-caused alterations in the cycles of either N or  
84 P (Vitousek et al. 1997, Bennett et al. 2001, Galloway et al. 2008) – and particularly of both  
85 together – have the potential to alter the dynamics of many ecosystems.

86 In this paper, we seek to identify and evaluate the mechanisms underlying global patterns  
87 in nutrient limitation. Earlier work by Vitousek and Howarth (1991; see also Vitousek and Field  
88 1999, Vitousek et al. 2002) sought to explain the variety of mechanisms that drive N limitation –  
89 addressing in particular the conundrum of the co-occurrence of widespread N limitation to  
90 primary production and the ubiquitous occurrence of organisms with the capacity to fix N

91 biologically from the unlimited supply of N<sub>2</sub> in the atmosphere. Accordingly, here we focus on  
92 the mechanisms that could cause or contribute to P limitation, and explore how the mechanisms  
93 driving P limitation relate to and interact with those driving N limitation.

#### 94 NUTRIENT LIMITATION CONCEPTS

95 Before addressing the mechanisms underlying P limitation in particular, we discuss a  
96 conceptual framework for nutrient limitation in general. At one level, the concept is  
97 straightforward – nutrient limitation occurs when meaningful additions of an essential element in  
98 biologically available forms cause an increase in the rate of a biological process (such as primary  
99 productivity) and/or in the size of an important ecosystem compartment (such as biomass).  
100 Nutrient limitation may be inferred by indirect measurements, of which the most common  
101 include: 1) nutrient availability in soil (Powers 1980); 2) plant investments in acquiring  
102 particular nutrients (Harrison and Helliwell 1974); and 3) tissue concentrations or ratios of  
103 elements (van den Driessche 1974, Koerselman and Meuleman 1996). The last of these is now  
104 the most widely used; it provided the basis for both Wardle et al.'s (2004) and Wassen et al.'s  
105 (2005) identification of P-limited ecosystems. Inferring nutrient limitation in this way –  
106 particularly identifying the more limiting nutrient, of N and P – should be robust when studies  
107 are carried out within a defined group of plants and ecosystems, and when they are calibrated  
108 with fertilization studies (Koerselman and Meuleman 1996). The approach can break down  
109 when applied across wide differences in phylogeny or climate; species (and regions) differ in  
110 their underlying N:P stoichiometry (for example, legumes are rich in N whether or not they  
111 actively fix N (McKey 1994)). In the end, nutrient limitation is defined operationally - by how  
112 primary production and other biological processes respond to added nutrients, as in the studies  
113 summarized by Elser et al. (2007) and LeBauer and Treseder (2008).

114 Our ability to understand nutrient limitation is complicated in practice by the pervasiveness  
115 of multiple resource limitation (MRL), which occurs when the addition of any one of several  
116 resources causes an increase in production and/or biomass. MRL can arise in a variety of ways –  
117 including physiological processes within plants, positive interactions in resource supply, and  
118 limitation of different species or functional groups within an ecosystem by different resources.  
119 On the physiological level, MRL probably represents the normal situation for terrestrial plants  
120 (Bloom et al. 1985, Field et al. 1992); indeed theoretical analyses suggest that to the extent  
121 possible, plants should adjust their physiology and morphology (through root-shoot allocation  
122 and reciprocal changes in resource use efficiency) such that they are limited simultaneously by  
123 multiple resources (Field et al. 1992, Rastetter et al. 1997).

124 MRL on the physiological/morphological level applies most clearly to resources that are  
125 acquired by distinct pathways, like light, carbon dioxide, and water or nutrients (Field et al.  
126 1992). However, MRL arising from positive interactions in resource supply clearly applies to  
127 nutrients like N and P that most plants obtain from soil through roots and mycorrhizae. The  
128 supply of P constrains rates of N fixation in many ecosystems (discussed further below), such  
129 that additions of P can increase the inputs and ultimately the availability of N in both aquatic  
130 (e.g. Schindler 1977) and terrestrial (e.g. Crews et al. 2000, Eisele et al 2002) ecosystems.  
131 Conversely, additions of N can allow organisms to produce more extracellular phosphatase  
132 enzymes that cleave ester-P bonds in soil organic matter (McGill and Cole 1981, Olander and  
133 Vitousek 2000, Treseder and Vitousek 2001, Wang et al. 2007) – increasing local availability of  
134 P. These interactions are not fully symmetrical; by affecting N fixation, P supply affects the  
135 quantity of N within ecosystems, while additional phosphatase enzymes affect the rate of cycling  
136 but not the quantity of P within ecosystems. However, within limits these and other interactions

137 can allow the supply of biologically available N and P to equilibrate, yielding many ecosystems  
138 in which plants are poised near the point where N and P are equally limiting – as illustrated by  
139 the summary by Elser et al. (2007).

140 Finally, MRL in diverse ecosystems can arise because increases in productivity or biomass  
141 stimulated by added nutrients may be unevenly distributed across plant species and functional  
142 groups. Species that have evolved toward different resource requirements may simultaneously  
143 be limited by and respond to different resources in a common environment, a situation that in the  
144 aggregate represents MRL (Gleeson and Tilman 1992).

145 Another challenge in applying the concepts underlying nutrient limitation is the distinction  
146 between proximate and ultimate limiting resources. We define a proximate limiting nutrient as  
147 one for which additions stimulate biological processes or pools directly, while an ultimate  
148 limiting nutrient is one capable of transforming ecosystems – typically by driving a substantial  
149 and persistent change in ecosystem structure and/or species composition as well as increasing the  
150 rates of biological processes. Studies of lake eutrophication by David Schindler and colleagues  
151 (Schindler 1971, 1977) illustrate this distinction as we define it (a different definition is current  
152 in marine biogeochemistry). Several decades ago, there was considerable controversy  
153 surrounding the components of human activity that cause lake eutrophication. Was it due to  
154 anthropogenic inputs of C? Of N? Of P? Each of those elements gets into lakes by different  
155 pathways, and experiments based on bioassays (in which these elements were added one at a  
156 time or in combination to bottles or microcosms containing lake water) found that each of them  
157 alone could stimulate primary productivity and algal growth in soft-water lakes. Consequently,  
158 all could be considered proximate limiting nutrients, and the lake water exhibited multiple  
159 resource limitation. However, longer-term whole lake experiments (summarized in Schindler

160 1977) demonstrated that only additions of P had the potential to convert many oligotrophic lakes  
161 into eutrophic ones. Phosphorus is an ultimate limiting nutrient here because additions of P  
162 cause inputs of N (by biological N fixation) and C (by enhancing CO<sub>2</sub> diffusion into lakes);  
163 together, these inputs of P, N and C transform oligotrophic lakes into eutrophic ones. In contrast,  
164 N and C are not ultimate limiting nutrients because adding them does not increase the input of P,  
165 and lakes remain oligotrophic.

166         Because primary producers are relatively long-lived in terrestrial ecosystems, ultimate  
167 limiting nutrients are difficult to identify on the time scale of fertilization experiments - even  
168 though both science and management may be more concerned with ecosystem transformation  
169 than with bounded increases in productivity. We believe one well-characterized example of  
170 ultimate limitation in terrestrial ecosystems is the transformation of many Northwestern  
171 European heathlands to productive grasslands, as a consequence of anthropogenically enhanced  
172 atmospheric deposition of N over a period of decades (Berendse et al. 1993). More generally, a  
173 combination of sustained whole-system experiments like those summarized by Schindler (1977,  
174 Schindler et al. 2008), long-term observational studies (including chronosequences), and  
175 fundamental understanding of the biogeochemical mechanisms that drive nutrient limitation can  
176 allow ultimate limiting nutrients to be identified and characterized.

#### 177                   MECHANISMS UNDERLYING PHOSPHORUS LIMITATION

178         We recognize 6 mechanisms that can cause P limitation to terrestrial ecosystems: P  
179 depletion, soil barriers, transactional, low-P parent materials, P sinks, and anthropogenic forcings  
180 (Table 1). These mechanisms are not alternative hypotheses – rather, multiple mechanisms can  
181 and do affect particular ecosystems both individually and interactively. To evaluate these  
182 mechanisms, and to determine the circumstances in which P can be an ultimate limiting resource,

183 we consider the dynamics of N and P simultaneously. While the limits within which N and P  
184 can equilibrate are constrained by their different sources, cycles, and dynamics, any process that  
185 increases the availability of either N or P makes it more likely that the other element will become  
186 limiting.

187 Throughout our exploration of mechanisms driving P limitation, we make use of the  
188 chronosequences summarized by Wardle et al. (2004); the use of chronosequences forces a long  
189 time perspective that is consistent with detecting and characterizing ultimate limiting nutrients.  
190 Moreover, the particular chronosequences they discuss can be used to illustrate several of the  
191 mechanisms we review here.

## 192 **Depletion-driven P limitation**

193 Perhaps the best-recognized cause of P limitation to terrestrial ecosystems is the  
194 progressive loss of P that can occur during long term soil and ecosystem development. We term  
195 this mechanism depletion-driven P limitation; together with soil sinks for P (below), it is a major  
196 component of the Walker and Syers (1976) model (Fig. 1). Depletion of P is evident in a  
197 chronosequence across the Hawaiian archipelago; by the oldest site on the sequence (4.1 million  
198 years), 90% of the P from parent material has been lost (Chadwick et al. 1999, Vitousek 2004) –  
199 much of it via leaching of dissolved organic P (Hedin et al. 2003). A long-term fertilizer  
200 experiment demonstrated that P supply limits both plant production and litter decomposition  
201 (Herbert and Fownes 1995, Hobbie and Vitousek 2000) in the oldest site, in contrast to younger  
202 sites on the sequence (Vitousek and Farrington 1997). After several years of fertilization, P  
203 additions induced secondary N limitation to plant growth in the oldest site (Harrington et al.  
204 2001) – and later still, the excess of P and relative dearth of N in P-fertilized plots led to a

205 spectacular bloom of N-fixing cyanolichens on trunks and in the canopy of this forest (Benner  
206 and Vitousek 2007).

207         In contrast to tropical areas, Pleistocene glaciations have ensured that few cold-temperate  
208 or high-latitude sites reach soil ages of 40,000 years, much less 4 million years, without having  
209 their parent material P rejuvenated or subsidized by glacial or periglacial processes. Consistent  
210 with this suggested geographical pattern, P limitation plays a more prominent role in tropical  
211 than in temperate agriculture (Sanchez 1976), and a substantial subset of lowland tropical forests  
212 have lower tissue P concentrations and much wider N:P ratios than do any temperate forests  
213 (Vitousek 1984, McGroddy et al. 2004). However, P depletion is not a feature of all tropical  
214 soils – volcanism, tectonic uplift, erosion, and other disturbances (besides glaciation) that can  
215 rejuvenate the supply of P from rock are as frequent in the tropics as the temperate zone (Bern et  
216 al. 2005, Porder et al. 2005a, b; 2007), and so many tropical forests and soils are relatively young  
217 and rich in P (Vitousek and Sanford 1986).

### 218 **Phosphorus limitation caused by the development of soil barriers**

219         Soil developmental processes other than depletion can contribute to P limitation by  
220 making portions of soils inaccessible or inhospitable to roots and thereby physically separating  
221 biota from P and P-bearing minerals. We term this class of mechanisms soil barrier-driven P  
222 limitation. A clear example occurs on chronosequences in permafrost-dominated regions; shade,  
223 organic soil horizons, and moss progressively insulate soils and allow permafrost to develop after  
224 several hundred years (Viereck et al. 1983) - isolating plants from deeper portions of the soil  
225 profile.

226         Other pedogenic soil barriers can influence P availability and limitation. Iron pans  
227 (placic horizons) that form in high-rainfall regions can constrain root access to deeper parts of

228 soil profiles and restrict drainage, routing water horizontally rather than vertically through soils  
229 and in high-rainfall sites causing soil saturation and anaerobiosis (McKeague et al., 1983,  
230 Kitayama et al. 1997). The development of clay-rich soil horizons can have similar  
231 consequences; Lohse and Dietrich (2005) demonstrated that a textural discontinuity associated  
232 with such a horizon routed most water horizontally in the P-limited oldest site of the Hawaiian  
233 chronosequences, and most roots in the site explore the area above that discontinuity (Ostertag  
234 2001). Finally, acidic, high-aluminum subsoils that form in many high-rainfall environments  
235 may permit water flow but serve as a barrier to the growth of roots towards deeper, more P-rich  
236 portions of soil profiles (Soethe et al. 2006).

237         By blocking root access to deeper soil horizons with P-containing minerals, barriers can  
238 have a greater effect on the supply of P than N, making limitation by P more likely. Additionally,  
239 anaerobiosis resulting from soil barriers slows decomposition and element cycling, and organic  
240 N and P can accumulate (Ugolini and Mann, 1979) – causing sink-driven limitation (discussed  
241 below). P is relatively mobile in anaerobic soils, because the ferric iron that forms insoluble  
242 complexes with P under aerobic conditions is reduced to soluble ferrous iron – potentially  
243 increasing the availability of P in the short run, but at the same time greatly increasing rates of P  
244 depletion (Miller et al. 2001, Thompson et al. 2006). To the extent that soil barriers promote  
245 shallow flowpaths through organic soils and high DON losses, N limitation may also be  
246 reinforced by barriers.

247         Overall, pedogenic barriers can cause rapid (hundreds to thousands of years) or slow  
248 (millions of years) reductions in the stature of vegetation (Simard et al. 2007). Soil barriers  
249 contribute to the low-stature, nutrient-limited vegetation observed on older marine terraces of the  
250 Mendocino chronosequence in California (Jenny et al. 1969), and probably also to low nutrient

251 availability in older muskeg sites of the Glacier Bay chronosequence summarized by Wardle et  
252 al (2004).

### 253 **Transactional P limitation**

254 Early in soil development, most P remains in primary minerals and P availability in soil  
255 may be low (Crews et al. 1995). Where biological N fixers are sparse and other N inputs are  
256 small, N availability will generally be even lower than that of P – and N supply is likely to limit  
257 plant growth, as is observed in young sites on the Hawaiian chronosequence (Harrington et al.  
258 2001, Vitousek 2004). However, where N fixers are abundant early in ecosystem development,  
259 as in the Glacier Bay chronosequence and many others, the resultant high N-P ratio of inputs can  
260 cause P limitation in young soils (Chapin et al. 1994). We term this mechanism transactional P  
261 limitation – abundant P is present in parent material, but it weathers slowly enough (and N and  
262 other resources are abundant enough) that P supply constrains plant growth. Transactional P  
263 limitation might be considerably more widespread were plants and mycorrhizae not able to  
264 increase the availability of P in soils by enhancing weathering rates (Blum et al. 2002, Hoffland  
265 et al. 2002) and by other pathways (Lambers et al. 2008). The potential importance of  
266 transactional P limitation is not confined to early soil development; as discussed below, either  
267 anthropogenic enrichment by N or very high rates of geological uplift and erosion can lead to  
268 transactional P limitation.

### 269 **Parent Material Based P Limitation**

270 The P content of different parent materials can differ by over two orders of magnitude  
271 (McBirney 1993). At the low end of this range, the quantity of P present in parent material as  
272 soils begin to develop can constrain plant growth and other ecosystem processes, a situation that  
273 we characterize as parent material based P limitation. A clear illustration can be drawn from the

274 quartzite sandstone rocks of the Cape Province, South Africa, that underlie portions of the  
275 notoriously P-poor fynbos biome; they contain less than 40 ppm total P (Soderberg and Compton  
276 2007), versus 700 ppm in average continental crust and 3000 ppm in particularly rich oceanic  
277 basalt (Taylor and McClennan 1985, McBirney, 1993). Parent material differences can be  
278 accentuated during soil development, in that basaltic soils tend to collapse over time and  
279 concentrate remaining elements whereas quartz-rich soils lose mass (and elements) from other  
280 constituent minerals but tend to retain their original volume because quartz weathers so slowly  
281 (White 1995). The Cooloola chronosequence summarized by Wardle et al. (2004) developed in  
282 quartz sand; its P dynamics likely reflect both parent material based and depletion driven P  
283 limitation (Walker et al. 1983).

284         The texture of parent material also can play an important role, one that fits between  
285 parent material based and transactional P limitation. Weathering is a surface-area-dependent  
286 phenomenon, and massive surfaces (rock faces) weather much more slowly than fine particles.  
287 Raich et al. (1996) contrasted the response of native vegetation to N versus P additions in three  
288 volcanic sites in Hawaii – one underlain by massive pahoehoe lava, one by rough cobbles of aa  
289 lava, and the third by much finer particles of volcanic cinder. All three were on young substrates  
290 and supported few N fixers, and all were limited by N more than by P. However, their response  
291 to P additions matched their parent material texture; tree growth following P addition was 62%  
292 of that following N addition in the low-surface-area pahoehoe site, 28% of the N response in the  
293 intermediate-texture aa site, and there was no effect of added P in the high surface area cinder  
294 site (Fig. 2).

295 **Sink-Driven P limitation**

296           The accumulation of meaningful quantities of an essential element into a growing pool  
297 within an ecosystem represents a withdrawal of that element from circulation, making limitation  
298 by that element more likely. We term this process sink-driven P limitation. The Walker and  
299 Syers model (Fig. 1) proposes that P limitation in ecosystems on old soils is caused by both  
300 depletion and sinks; they suggest that an increasing fraction of the P that remains within ancient  
301 soils is bound in occluded (insoluble and/or physically protected) forms that are not accessible to  
302 organisms. In the Hawaii chronosequence, 90% of parent material P had been lost, and about  
303 half of the remaining P in the oldest site was found in occluded forms (Crews et al. 1995,  
304 Chadwick et al. 1999, Vitousek 2004).

305           The importance of sinks for P versus N limitation depends on the nature of the sinks.  
306 Strong adsorption of P on colloids and its precipitation with iron, aluminum, manganese, or  
307 calcium represent substantial sinks for P – and not N – in many soils. This adsorption and  
308 precipitation of P could compete with organisms for available P in the short term (Olander and  
309 Vitousek 2004), and represent an accumulating sink of P in the longer term. Such inorganic  
310 sinks drive biological processes towards P limitation in a wide variety of soils, though by  
311 differing pathways – for example by precipitation with Ca in aridland soils or with free iron and  
312 aluminum in podsoles, or by adsorption onto allophane or sesquioxides in many tropical soils  
313 (Uehara and Gillman 1988).

314           Where living biomass represents an accumulating sink (Miller 1976, Rothstein et al.  
315 2004), its N:P stoichiometry should be similar to that of organisms' requirements. However,  
316 where the sink is litter or soil organic matter, biochemical (phosphatase-mediated) mineralization  
317 of P (McGill and Cole 1981) could regenerate P more rapidly than decomposition can regenerate  
318 N – and so all else being equal, a soil organic matter sink could drive systems towards N

319 limitation. In high-rainfall areas where accumulated soil organic matter increases water holding  
320 capacity and slows drainage, the consequent soil saturation and anaerobiosis can feed back to  
321 enhance organic matter accumulation (Van Breemen, 1995). This feedback increases the sink,  
322 but it could also bring other processes to bear – including enhanced mobility of P and N, and  
323 potentially loss of contact with underlying mineral-soil horizons - as discussed above for soil  
324 barrier-driven limitation.

### 325 **Anthropogenic P Limitation**

326         Just as human activity can transform P-limited ecosystems by adding P (Schindler 1977),  
327 human activity can induce P limitation by purposefully or inadvertently affecting the supply of  
328 other resources, most often N. We call this mechanism anthropogenic P limitation. For  
329 example, extraordinarily high levels of atmospheric N deposition in northwestern Europe have  
330 overwhelmed N limitation in many sites (Berendse et al. 1993, Stevens et al. 2004), and many of  
331 the altered systems are now limited primarily by P (Fig. 3) (Verhoeven and Schmitz 1991, Aerts  
332 et al., 1992). Similar results have been obtained in controlled experimental settings in North  
333 America (Tilman 1987, Huenneke et al. 1990, Suding et al. 2007). Fertilization experiments  
334 further demonstrate that adding N can increase the rate at which P cycles, by allowing organisms  
335 to produce more extracellular phosphatase enzyme and thereby release phosphate from soil  
336 organic matter (Olander and Vitousek 2000, Treseder and Vitousek 2001); a similar stimulation  
337 of P cycling occurs in areas receiving high levels of anthropogenic N deposition (Gress et al.  
338 2007). However, the increase in P cycling observed in N-fertilized sites typically is insufficient  
339 to balance the increased rate of N inputs, and P often becomes limiting.

340         Human-enhanced N deposition now is concentrated in Europe, central and eastern North  
341 America, east Asia, and peri-urban areas elsewhere (Galloway and Cowling 2002). Ecological

342 experiments (and ecologists) are concentrated in the same areas, and it is possible that much of  
343 the P limitation summarized in the meta-analysis by Elser et al. (2007) reflects anthropogenic P  
344 limitation secondary to human alteration of the N cycle. Conversely, human alterations of the  
345 global P cycle could cause anthropogenic N limitation – certainly in P-fertilized ecosystems  
346 where N fixation is constrained, possibly where land use causes widespread increases in the  
347 long-distance transport of atmospheric dust (Okin et al. 2004, Tegen et al. 2004). The greater  
348 mobility and biological availability of combined N in the atmosphere implies that anthropogenic  
349 P limitation should be much more widespread (if perhaps less persistent) than anthropogenic N  
350 limitation.

## 351 DISCUSSION

352 The mechanisms that individually and interactively drive P limitation - together with  
353 those driving N limitation, which are summarized in Table 2 – could contribute to our  
354 understanding of N and P dynamics in terrestrial ecosystems in two ways. First, we are  
355 concerned with nutrient limitation (both proximate and ultimate) to many more ecosystems than  
356 we will be able to test empirically with fertilization. Indirect measures like element ratios in  
357 foliage can be useful predictors of which nutrient is likely to limit particular sites, and so to  
358 which anthropogenic changes particular systems are likely to prove most vulnerable. However,  
359 the inferences derived from such indices will be much stronger if they are coupled to  
360 mechanism-based understanding of why those particular nutrients are limiting to particular  
361 ecosystems.

362 Second, identifying ultimate limiting nutrients is important, because alterations in their  
363 supply have the capacity to transform the structure and functioning of ecosystems. The long-  
364 term, well-controlled, whole-system experiments that are necessary to establish ultimate versus

365 proximate limitation (Schindler et al. 2008) will always be sparse, particularly in terrestrial  
366 ecosystems with perennial vegetation. It will be largely through the understanding of  
367 mechanisms that we can build upon those few experiments to determine where particular  
368 nutrients are likely to represent ultimate limiting resources, and why.

369         Which of the mechanisms driving P limitation are capable of causing ultimate P  
370 limitation? Clearly, P depletion in ancient, deeply leached soils can drive ultimate P limitation –  
371 just as Walker and Syers (1976) implied when they described such soils as being a “terminal  
372 steady state” of profound P limitation, from which there is no exit other than geological  
373 disturbance or human fertilization that can rejuvenate soils. Parent material based P limitation  
374 also can be deep and sustained. Where soil barriers develop into permanent features of soils  
375 (permafrost prior to rapid global warming; massive placic horizons in some tropical soils), they  
376 too could drive ultimate P limitation by physically constraining the volume of the biologically  
377 accessible portion of the ecosystem.

378         In contrast, most forms of sink-driven P limitation are transitory, leading to proximate  
379 limitation; sooner or later most sinks become saturated, unless another process removes P from  
380 the system. The occluded P accumulated in ancient soils (Fig 1) (Walker and Syers 1976) may be  
381 an exception, although recent evidence suggests that much of that pool is dynamic on decadal  
382 time scales (e.g. Richter et al. 2006). Most often, transactional P limitation is similarly  
383 transitory; generally it occurs when other resources (particularly N) are supplied rapidly enough  
384 that even though P is present in primary minerals, its supply via weathering cannot keep up.  
385 Except where erosion is extremely rapid (discussed below), P supplied via weathering should  
386 accumulate in biologically-available pools and eventually bring the supply of P more or less into  
387 alignment with other limiting resources. Anthropogenic P limitation should behave similarly to

388 transactional limitation; in many (not all) situations, it is a special case of transactional  
389 limitation.

390 We conclude that the most important mechanisms causing ultimate P limitation are those  
391 that affect the ecosystem-level mass balance of P. No terrestrial ecosystem is closed – even for a  
392 relatively immobile element like P – so an essential component of the maintenance of any low-P  
393 terminal steady state is losses of P. Mechanisms involving depletion, physical barriers, and low-  
394 P parent material all depend on the existence of pathways of P loss that continue even where P is  
395 limiting to organisms, and which thereby prevent accumulation of biologically available P from  
396 very small inputs via continued weathering or dust fluxes (Chadwick et al. 1999, Okin et al.  
397 2004, Soderberg and Compton 2007). Losses via dissolved organic P could fulfill this condition  
398 (Hedin et al. 2003). In effect, the depletion-driven mechanism summarizes the situation during  
399 soil development in which losses of P are greater than inputs via weathering and other pathways  
400 – until the terminal steady state is reached, and inputs and outputs are both very small. Limitation  
401 based on soil barriers works similarly but can develop more rapidly; only processes occurring in  
402 the constrained space above the barrier are relevant to terrestrial biota, and these can come to a  
403 terminal steady state more rapidly. In parent-material based limitation, inputs of P are low from  
404 the very early stages of soil development onward, and even very small losses of P can offset  
405 weathering.

406 An ecosystem-level steady state in P need not be the terminal steady state described by  
407 Walker and Syers (1976). The uplift/erosion model of ecosystem P balances by Porder et al.  
408 (2007) showed that moderate rates of uplift and erosion (typical of much of Earth's surface)  
409 should yield inputs of P via uplift and losses via erosion and other pathways that are more or less  
410 in balance, under circumstances that (for most parent material P contents) should provide a

411 sufficient supply of P to terrestrial ecosystems. Ultimate limitation by P generally arises with  
412 very slow rates of erosion, which make depletion-driven and soil barrier limitation possible. On  
413 the other hand, very rapid uplift and erosion could cause losses via erosion to occur before much  
414 weathering of primary minerals can take place - preventing the accumulation of a biologically  
415 available pool and thereby allowing transactional P limitation to cause ultimate limitation.

416         We have focused on the mechanisms driving P limitation here – but N limitation could be  
417 proximate or ultimate as well. Without using this terminology, Vitousek and Field (1999)  
418 suggested that limitation by N could be an ultimate control over primary productivity only when  
419 each of two ecosystem mass balance conditions is met. First, there must be a pathway of N loss  
420 that cannot be controlled by biological activity, even when N is in short supply. Persistent losses  
421 of dissolved organic N from undisturbed ecosystems can satisfy this condition (Hedin et al. 1995,  
422 Perakis and Hedin 2002), as can losses associated with frequent disturbance (Houlton et al. 2003,  
423 Vitousek 2004). These disturbance-associated losses should play a larger part in the development  
424 of N than of P limitation, because the high mobility of N means that N losses can be substantial  
425 whenever the supply of biologically available N exceeds demand, even briefly. Indeed, Davidson  
426 et al. (2007) recently demonstrated that N losses associated with human disturbances to  
427 putatively P-limited Amazonian ecosystems altered their N/P stoichiometry sufficiently to induce  
428 limitation by N in secondary forests. Where fire is an important agent of disturbance, it  
429 reinforces the likelihood of N limitation; fire in particular volatilizes much more N than it does  
430 P.

431         Second, for N to be an ultimate limiting nutrient there also must be constraints to  
432 biological N fixation that cannot be overcome even when N is limiting to primary production.  
433 Major constraints that have been identified include the energetic cost of fixing N (especially

434 under a plant canopy), differential grazing on protein-rich N fixers, the supply of P and of trace  
435 elements associated with the biochemistry of N fixation (Vitousek and Howarth 1991, Vitousek  
436 and Field 1999), and low temperatures (Houlton et al. 2008). Where the supply of P is a major  
437 constraint to N fixation, proximate limitation by N can be a manifestation of ultimate limitation  
438 by P.

439 For both N and P, understanding the controls of ecosystem mass balances is crucial to  
440 identifying and characterizing ultimate limiting nutrients – as Schindler’s studies of lake  
441 eutrophication demonstrate (Schindler 1977). On land, the cycles of N and P are coupled  
442 through biological demand – but they differ so substantially in sources and dynamics that either  
443 element may be or may become in short supply compared to the other. As human activities  
444 continue to increase N inputs across more of Earth’s surface, some areas will continue to be  
445 transformed by that added N. In others, limitation by P or other resources will develop, or  
446 become deeper and more widespread.

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676 Table 1. Pathways, mechanisms, and time scales of P limitation to primary production in  
 677 terrestrial ecosystems. See text for descriptions and references.

678	Pathway	Mechanism	Time Scale (yrs)
679	Depletion-Driven	Loss of inorganic and dissolved organic P	millions
680		via leaching; exhaustion of primary	
681		minerals in soil	
682	Soil Barrier	Formation of soil layers that physically	hundreds to tens
683		prevent/inhibit access by roots to potentially	of thousands
684		available P	
685	Transactional	Slow release of P from mineral forms, relative	decades to
686		to the supply of other resources	centuries
687	Low-P Parent	Low inputs of P via weathering due	all – develops
688	Material	to low concentrations of P in rock	quickly and
689			persists
690	Sink-Driven	Sequestration of available P in an	decades to
691		accumulating pool within ecosystems	millennia
692	Anthropogenic	Enhanced supply of other resources (especially	years to decades
693		N) causes P limitation	
694			

694 Table 2. Pathways, mechanisms, and time scales of N limitation to primary production in  
 695 terrestrial ecosystems; information from Vitousek and Howarth (1991), Vitousek and Field  
 696 (1999), and Vitousek (2004).

697	Demand-Indepen-	Losses of combined N that organisms cannot	decades to
698	dent Losses	prevent – including leaching of DON, post-	centuries;
699		disturbance losses, some gaseous pathways	depends on
700			loss pathway
701	Constraints to	Biological N fixation is slow or absent even	decades to
702	Biological N	when N is limiting; could be due to energetic	centuries
703	Fixation	costs, differential grazing, demands for P, Mo	
704		or other essential elements	
705	Transactional	Slow release of N from complex organic into	years to centuries
706		soluble forms, relative to the supply of other	
707		resources.	
708	Sink-Driven	Sequestration of available N in an	decades to
709		accumulating pool within ecosystems	millennia

## FIGURE LEGENDS

710

711 Fig. 1. Changes in the pools and overall quantity of P in ecosystems over the course of soil  
712 development, based on Walker and Syers (1976).

713 Fig. 2. The effect of the texture of parent material on the extent of P limitation to plant growth in  
714 young volcanic sites in Hawaii. Forests on coarse pahoehoe lava, intermediate-texture aa lava,  
715 and fine volcanic cinder all respond most strongly to additions of N plus P – but the effect of  
716 added P (alone) is strongest in the coarse-textured site, where low surface area slows weathering;  
717 the effect of P is intermediate on the intermediate parent material texture, and absent in the  
718 finest-textured substrate. The fine-textured substrate supports the greatest particle surface area  
719 where weathering can take place. From Raich et al. (1996).

720 Fig. 3. Response of *Sphagnum* growth to additions of two levels (low and high) of N and P in a  
721 bog in southern Sweden that received high levels of anthropogenic N deposition (high-N site),  
722 and one in northern Sweden that received little anthropogenic N. C = control, LN and HN low  
723 and high N additions, and LP and HP low and high P additions. Redrawn from Aerts et al.  
724 (1992)





