

A leaky model of long-term soil phosphorus dynamics

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[1] Soil phosphorus (P) leaks rapidly from newly formed land surfaces to upland rivers and lakes, surface water P concentrations peaking early before declining as soil apatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) becomes depleted. We present lake sediment P profiles that record this leakage through the early Holocene. The results are entirely consistent with our re-analysis of published soil chronosequence data, but conflict with more recent quantitative interpretations of global soil P dynamics that identify far slower loss rates. P inherited from the bedrock on soil formation, long regarded as the major source for terrestrial ecosystems, only lasts $\sim 10^4$ years rather than the previously suggested 10^6 years, and thus is, globally, much less important in the long term than atmospheric supply. This changes the conceptualization of terrestrial P dynamics, with the “terminal steady state” of Walker and Syers (1976) being the norm not the exception, and with soil P export being little if at all controlled by biotic retention mechanisms. High early export of P from newly formed soil causes a peak in the productivity of terrestrial surface waters, before a decline as the soil P pool depletes. Globally, the $18 \times 10^6 \text{ km}^2$ of terrain exposed since the Last Glacial Maximum potentially produced a substantial surge in runoff P, with greatest impacts likely in high-latitude, restricted basin seas and maximal area of deglaciated terrain.

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1. Introduction

[2] Many studies have argued that soils in noneroding settings acquire most, if not all, of their phosphorus (P) from bedrock or unweathered surface materials during initial soil formation [Ruttenberg, 2003; Smeck, 1973], a geological P dose that undergoes transformation from primary to secondary forms [Walker and Syers, 1976], but which leaks away so slowly that it remains the dominant ecosystem P source until soils are $\sim 10^6$ years in age [Chadwick *et al.*, 1999; Crews *et al.*, 1995; Hedin *et al.*, 2003; Porder *et al.*, 2007]. In this conceptual model, the atmospheric P flux plays a minor role except at extremely old and mechanically noneroding sites [Porder and Hilley, 2011; Porder *et al.*, 2007] and even then serves only to minimize the state of P depletion, in what Walker and Syers [1976] call the “terminal steady state.” The ecological consequences of this interpretation of long-term soil P dynamics have been examined at several sites [Chadwick *et al.*, 1999; Hedin *et al.*, 2003; Richardson *et al.*, 2004], leading to the view that P export is bioregulated, leakage being initially high when primary productivity is nitrogen limited, and then progressively lower as P limitation becomes

increasingly severe. Regardless of the ecological mechanism, there is good evidence that P limitation can impact terrestrial productivity [Birks and Birks, 2004; Chadwick *et al.*, 1999; Richardson *et al.*, 2004; Wardle *et al.*, 2004], and the models of Porder *et al.* [2007] and Porder and Hilley [2011] allow us to predict where such limitation should occur.

[3] These model predictions are at their most reliable in rapidly eroding landscapes, where advective processes dominate. In stable landscapes, their predictions depend more on the decay rate of soil available P, and these are less well constrained, the analysis of Porder *et al.* [2007] finding rate parameters for different sites that differ by more than an order of magnitude. Furthermore, the magnitude of the estimated decay parameters found for available P by Porder *et al.* [2007] and for total P by Porder and Hilley [2011] is incompatible with the global riverine dissolved P flux of 6.7 to 12.1 $\text{mg m}^{-2} \text{ a}^{-1}$ of Ruttenberg [2003]. Even if all the decayed P were exported to runoff (rather than partially retained in the soil in unavailable forms), the decay constant of $2.9 \times 10^{-7} \text{ a}^{-1}$ would imply a mean soil P content of 27–41 kg m^{-2} , which is 2 orders of magnitude too large. In order to identify the source of this discrepancy and to better constrain long-term soil P dynamics in noneroding landscapes, we re-evaluate and develop the long-term, large-scale soil P model of Porder *et al.* [2007]. We do this by more explicitly assessing the dynamics of soil apatite and by supplementing the published soil chronosequence data with evidence from lake sediment records of runoff P, broadening the basis for parameterization and model validation. Such a refinement also allows us to consider the fate of P leaking from the soil; whether it is retained deeper in the soil or exported to runoff has profound implications for aquatic ecosystems.

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Table 1. Model Parameters and Coefficients

Parameters	Units	Description
P_T, P_{Ca}, P_S	g kg^{-1}	Soil concentrations of total (T), apatite (Ca), and secondary (S) P
D_{PT}, D_{PCa}, D_{PS}	g m^{-2}	Soil areal density of total (T), apatite (Ca), and secondary (S) P
Q_{atm}	$\text{g P m}^{-2} \text{a}^{-1}$	Supply to the soil surface of atmospherically derived P
Q_{supply}	$\text{g P m}^{-2} \text{a}^{-1}$	Supply of P to the soil from P_{Ca} dissolution and Q_{atm}
$Q_{leakage}$	$\text{g P m}^{-2} \text{a}^{-1}$	Total P export rate from the soil
P_{MAR}	$\text{g P m}^{-2} \text{a}^{-1}$	Mass accumulation rate (MAR) of non-apatite P in the lake sediment normalized to lake area
Coefficients		
k	a^{-1}	Rate coefficient for apatite dissolution
λ	a^{-1}	Rate coefficient for release of P_S
α	dimensionless	Fraction of P released directly to runoff on dissolution of apatite

[4] Previous models of soil P evolution over time have not incorporated data from lake sediments, which in some cases can preserve information about the evolution of soil P in the landscape over time. *Mackereth* [1966] observed that for three sites in the English Lake District, concentrations of P in lake sediments showed an early post-glacial maximum and subsequent decline. He argued that changing P supply from the catchment soil was the most likely cause, post-glacial warming bringing about an initial increase in weathering, and subsequent depletion of the soil P pool leading to an eventual decline. This interpretation in terms of fluxes was confirmed for Lake Trummen in southern Sweden by *Digerfeldt* [1972] who showed a maximum flux to the lake bed of 290–330 $\text{mg P m}^{-2} \text{a}^{-1}$ in the early Holocene, falling rapidly to 15–25 $\text{mg m}^{-2} \text{a}^{-1}$ within 3000 years. Higher-resolution Holocene P flux studies at Plešné Lake in the Czech Republic [*Kopacek et al.*, 2007] and Sargent Mountain Pond in Maine, USA [*Norton et al.*, 2011], provide greater detail, showing a rapidly increasing flux to the lake bed through the first 500–1000 years of the Holocene, followed by an exponential decrease up to the time of modern landscape disturbance. As observed by *Filippelli and Souch* [1999] based on low-resolution lake sediment records from North America, the decline stage of these curves shows striking similarity to the total soil P depletion trajectories of the *Walker and Syers* [1976] conceptual model, suggesting that lake sediments and soil chronosequences may share a common controlling mechanism. Crucially, lake sediment records provide a means of answering the question posed by *Walker and Syers* [1976] of where P leaked from soils ends up. Furthermore, lake sediments capture not only the soil P leakage but also eroded soil primary minerals from which the changing soil composition may be inferred (secondary soil minerals are also captured, though often less effectively owing to the small particle size). Thus, *Filippelli and Souch* [1999], *Norton et al.* [2011], and *Kopacek et al.* [2007] have used lake sediment records to reconstruct the history of soil apatite variation, and it is the dual function of providing records of both P export flux and soil apatite loss that we use lake sediment data for here.

2. Methods

2.1. Conceptual Model

[5] Our long-term soil P model comprises a simple numerical representation of the *Walker and Syers* [1976] conceptual model. It broadly follows the treatment of *Porder et al.* [2007], though simplified to a vertically integrated form. The long-term dynamic model of soil available P (here

designated as P_S , mg g^{-1}) presented by *Porder et al.* [2007] explores the balance between loss of available P due to a combination of leaching and immobilization and its supply from dissolution of apatite P (here designated as P_{Ca} , mg g^{-1}) either inherited from the original substrate or released via erosion-driven bedrock exhumation. Rates of release from apatite to the available P pool, and loss from it, are handled by the first-order rate constants (year^{-1}), with symbols k and λ , respectively. The model of *Porder et al.* [2007] assesses the role of exhumation relative to substrate inheritance in controlling the availability of P to ecosystems, quantifying the coefficients by the inverse method using noneroding chronosequences sites. *Porder and Hilley* [2011], in contrast, explore the relative importance of dust flux and exhumation the long-term regulation of soil total P (here designated as P_T , mg g^{-1}). They apply a similar model, but one in which the time scale makes it unnecessary to separate P_{Ca} from P_S , allowing the k term to be ignored. Again, this is calibrated using noneroding soil chronosequences data.

[6] For our investigation, which places greater emphasis on the early dynamics, we cannot ignore k , and in this sense, our model is close to that of *Porder et al.* [2007]. However, we differ from this study in ignoring the exhumation component which is done for two reasons. First, our focus on the early stages makes it less reasonable to adopt an assumption of steady state between erosion and exhumation [*Porder et al.*, 2007], which would require instead the use of a more complex but untestable dynamic erosion model. Second, the sites we use to parameterize our model (lake sediment records and the soil chronosequences) are from minimally eroding sites which therefore provide no guidance on parameterization of an erosion term. Consequently, our model is applicable only to sites with low exhumation rates. We estimate soil erosion at both lake study sites to be no more than 3 mm kyr^{-1} (bedrock equivalent). We assume that the soil chronosequence sites have experienced no soil erosion.

[7] We differ in one further way from both *Porder et al.* [2007] and *Porder and Hilley* [2011]. Because of our emphasis on absolute rather than relative fluxes, we express our model in terms of P density rather than concentration. Thus, our three concentration terms, P_T , P_{Ca} , and P_S , (in mg g^{-1}) have corresponding density terms D_{PT} , D_{PCa} , and D_{PS} (in g P m^{-2}). Fluxes associated with these P densities can be calculated directly using first-order rate constants. These terms and their units are listed in Table 1.

[8] Other differences are addressed in the text below. The field and laboratory data used to parameterize the model are obtained largely from published studies. The most important

Table 2. Lake Catchment Physical and Soil Properties Data

Parameter	Kråkenes Lake ^a	Sargent Mountain Pond ^b
Sediment accumulation area (SAA; km ²)	0.055	0.0038 ^c
Catchment area (CA; km ²)	0.814	0.02
Lake P loss correction factor (<i>F</i>)	1.83	1.24
Soil areal density (kg m ⁻²)	300–600	≤600
Initial P _{Ca} (mg g ⁻¹)	0.69	0.24–0.38

^aThis study.^bPerry [2007].^cTaken as half the total lake area [Rippey *et al.*, 2008].

methodological issues concern characterization of the soil and sediment P fractions, which differ somewhat among the various studies. Of the many operationally defined soil P fractions, two measured concentrations are both reproducible and useful to this study: acid-extractable P (P_{Ca}) which is assumed to be predominantly from apatite (Ca₅(PO₄)₃(OH)) [Walker and Syers, 1976] and total P (P_T) from which changes in soil profile P content can be calculated. Secondary soil P (P_S) is calculated as the difference between these two concentrations. Here P_{Ca} is the fraction removable by 0.5 M H₂SO₄ [Walker and Syers, 1976] or 1 M HCl [Crews *et al.*, 1995; Norton *et al.*, 2011] from the soil or sediment residue following extractions with 0.1 M NaOH and Na bicarbonate/dithionite [Psenner *et al.*, 1988]. P_T is normally calculated from the sum of all fractions including boiling concentrated H₂SO₄ [Crews *et al.*, 1995], 1 M NaOH at 85°C [Norton *et al.*, 2011], or NaCO₃ fusion followed by extraction with H₂SO₄ [Walker and Syers, 1976]. For the Kråkenes Lake sediment (site described below), P_T was measured by X-ray fluorescence analysis. The soil P fractions and model parameters used in this study are defined in Table 1.

2.2. Lake Study Sites

[9] Two lakes sites were used for this research. Kråkenes Lake, situated 38 m above sea level on the island of Vågsøy, Western Norway, a small (0.055 km²) lake with a catchment mainly of mixed granitic and amphibolitic rocks, was formed by deglaciation approximately 14 ka B.P. (see Boyle *et al.* [2013] for details). Sargent Mountain Pond, situated at 336 m above sea level in Acadia National Park, Maine, USA, a very small (0.0038 km²) lake with a granitic catchment, was formed by deglaciation approximately 16 ka B.P. (data from Perry [2007]).

2.2.1. Coring, Chronology, and Elemental Analysis

2.2.1.1. Kråkenes Lake

[10] Full details on the procedures summarized here are given in Boyle *et al.* [2013]. A sediment core (8.96 m) was collected from the terrestrialized southwestern lake arm (lake level was lowered in the nineteenth century) using a 1 m long 70 mm diameter Russian corer in 10 overlapping drives in May 2007. Meter-long sections were stored at 4°C in plastic guttering, wrapped in polythene sleeves. Within 2 weeks, the core drives were sliced at 1 cm intervals and freeze dried. Loss on ignition at 450°C was measured relative to the dry weight at 105°C. The total element concentrations were determined by X-ray fluorescence (XRF) analysis using a Bruker S2 Ranger energy dispersive instrument. Loose powders were pressed lightly in sample cups with 6 μm polypropylene film

and were measured for 250 s under helium at three different tube settings. Variable alpha mass attenuation corrections were applied taking measured organic matter concentrations into account. Calibration used a set of 15 certified reference materials, and processing the reference materials as unknowns generated root mean square differences for P of better than 5% of the mean. The allogenetic phosphorus fraction was measured by XRF analysis after chemical treatment to remove loosely bound and organic fractions, using 1 M NaOH, based on the modified Williams method of Pardo *et al.* [1999]. Core chronology was established using tephra layers (Vedde 11.97–12.25 ka, Saksunarvatn 10.11–10.25 ka, and Hekla-4 ~4.4 ka) and cross correlation with the radiocarbon-dated master core for Kråkenes [Birks *et al.*, 2000].

2.2.1.2. Sargent Mountain Pond

[11] Full details are given in Perry [2007]. A 5.3 m long core was taken from the center of the lake (5 m water depth) using a 1 m long, 50 mm diameter square-rod piston corer in six overlapping drives in March 2007. The core was sectioned in the field at 20 mm intervals. The sediment was stored at 4°C. Phosphorus was fractionated using the method of Lukkari *et al.* [2007]. Only the apatite (HCl extractable) and available (NaOH extractable) fractions are reported here. Twelve AMS (Accelerator Mass Spectrometry) ¹⁴C measurements (primarily plant macrofossils) ranging 2900 to 13,300 ¹⁴C years were used to develop an age-depth model.

2.3. Lake Sediment Record of Soil P Export

[12] Our model assumes (a) that P leaked from soil is exported in runoff and (b) if a lake intercepts such runoff, then it captures a proportion of the leaked P. Thus, lake sediment records of P flux can be used to investigate soil P leakage, provided corrections can be made for incomplete P retention by the lake, and for the magnification effect of a larger catchment feeding into a smaller lake. Equation (1) provides a simple procedure for linking the non-apatite P sedimentation flux (P_{MAR}, g m⁻² a⁻¹) at a coring site in the lake centre to the catchment soil P leakage flux (Q_{leakage}).

$$Q_{\text{leakage}} = P_{\text{MAR}} \times F \times \text{SAA}/\text{CA} \quad (1)$$

[13] *F* is a lake P retention factor that can be estimated from the empirical equation of Kirchner and Dillon [1975] (which predicts 1/*F* from water flux data), SAA (sediment accumulation area) is the area of lake bed within the mud limit [Rowan *et al.*, 1995] on which fine lake sediments accumulate (and across which P is assumed to accumulate evenly), and CA is the terrestrial catchment area. The data needed for these calculations are provided in Table 2.

[14] The scaling achieved by equation (1) has the effect of expressing the lake sediment flux record in a metric comparable to the soil P density. If Q_{leakage} calculated this way is expressed cumulatively (forward in time), and is normalized to the soil initial P_{Ca} density (D_{PCa,0}), then we obtain a measure changing soil P loss through time, starting at zero and increasing as the soil depletes. Thus, the percentage soil P loss at time *t* is given by

$$\text{percentage P loss}_t = 100 \frac{P_{\text{MAR,cumulative},t}}{D_{\text{PCa},0}} \quad (2)$$

[15] The calculations in equations (1) and (2) are based on the sediment record of non-apatite P. However, there is an

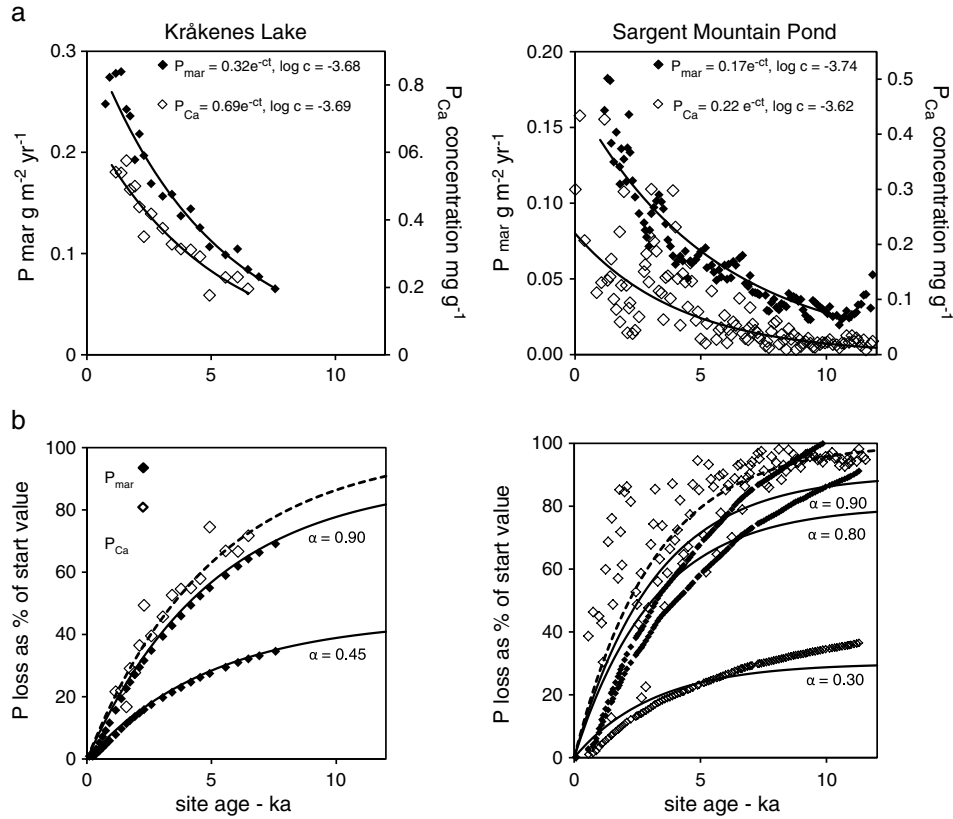


Figure 1. Lake sediment records of phosphorus at Kråkenes Lake, Norway, and Sargent Mountain Pond, Maine, USA. (a) Apatite concentration and phosphorus mass accumulation rate (MAR) values with best fit exponential curves and their rate constants, c . (b) Percent loss of apatite relative to the initial amount and gain by the lake sediment of exported soil phosphorus, expressed as percent loss of soil phosphorus relative to the initial total soil pool.

additional sediment P signal resulting from the presence of in-washed (allogenic) primary apatite [Boyle *et al.*, 2013]. As weathering depletes the soil of its apatite, the concentration of apatite present in the sediment allogenic fraction (as measured by sediment P_{Ca} normalized to the proportion of the sediment comprising allogenic matter) falls proportionately. The percentage apatite loss from the parent soil for time t is then estimated by

$$\text{apatite loss}(\%)_t = \frac{100(P_{Ca,0} - P_{Ca,t})}{P_{Ca,0}} \quad (3)$$

3. Results and Discussion

3.1. Lake Sediment Records of Long-Term Terrestrial P Fluxes

[16] The lake sediment records of Sargent Mountain Pond and Kråkenes Lake (Figure 1a) show broadly exponential declines in both apatite concentration (corrected for dilution by organic matter and biogenic silica using immobile elements [Boyle *et al.*, 2013]) and non-apatite P flux values. Both signals postdate the rapid early Holocene reduction in erosion rate and therefore are not driven simply by landscape stabilization. To assess the rates of decline, it is convenient to reverse the time axis, establishing a zero point after which weathering is

assumed to be active. In both cases, we have zeroed time at the start of the Holocene on the basis that any pre-Holocene weathering was at a substantially lower rate. At Kråkenes Lake, glacial ice covered a large part of the catchment to within a few decades of this date, and non-ice-covered ground experienced very low summer temperatures and precipitation [Birks *et al.*, 2000]. At Sargent Mountain Pond, the catchment had been ice free for some thousands of years, but remained cold during the Younger Dryas [Borns *et al.*, 2004]. The first-order rate coefficients calculated on this basis (Figure 1a) are similar for both lakes and for both phosphorus forms. This result is fully consistent with the soil P model of Walker and Syers [1976] in finding that leakage of P from the soil closely parallels depletion of apatite from the soil. To test this association, we calculate for the two sites both the rate of apatite loss from soil as inferred from P_{Ca} in the lake sediment (equation (3)) and the rate of decline in soil P leakage as inferred from the declining P flux to the sediment (equation (2)).

[17] The calculated percent loss of apatite (Figure 1b) follows a saturation exponential form. The percent total loss curves mirror the apatite loss closely in form, but lower in value reflecting partial retention of P in the soil. Several curves are shown for each lake representing the range of values estimated for the soil initial $D_{P_{Ca,0}}$. These curves suggest very substantial loss of soil P by the end of the Holocene, ranging 35–75% at Kråkenes Lake. At Sargent Mountain Pond, both curves suggest near-complete loss of initial soil P within the

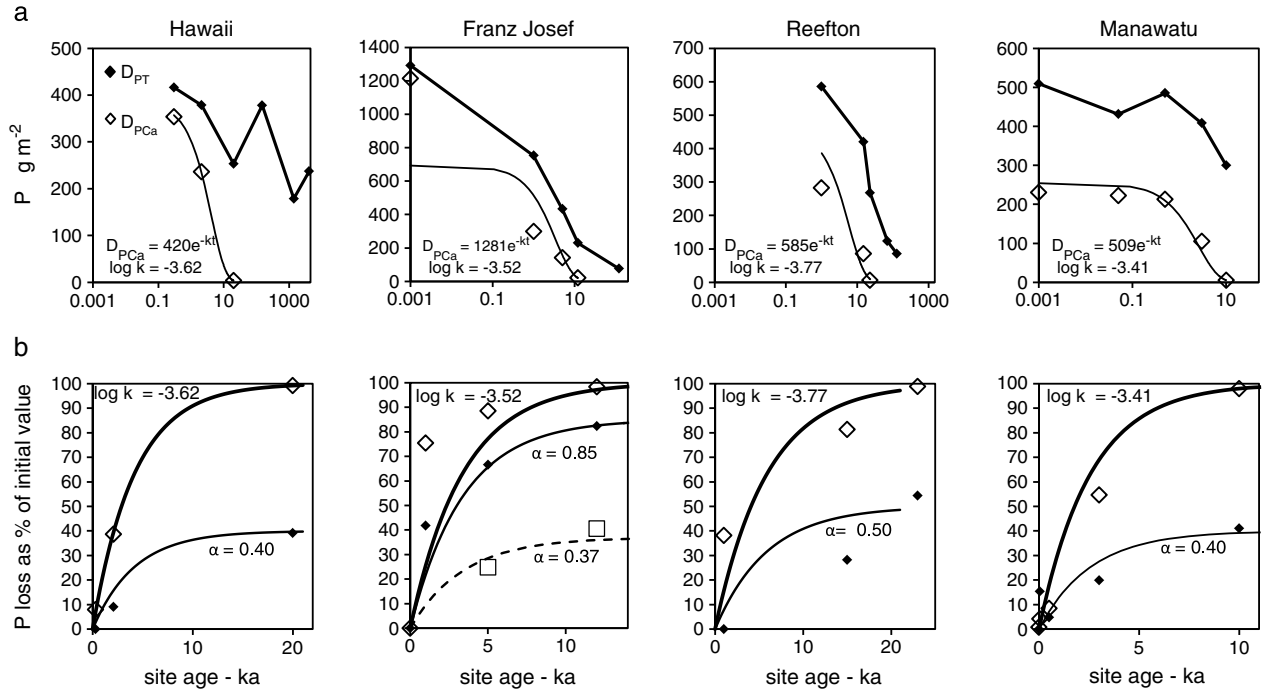


Figure 2. Soil chronosequence data for soil phosphorus dynamics at Hawaii, USA, and Franz Josef, Reefton, and Manawatu in New Zealand. (a) Apatite concentration and total phosphorus concentration (except Hawaii, which is P_T minus P_{occluded} [Porder *et al.*, 2007]). Best fit exponential curves and rate coefficients are shown for the apatite concentration. (b) Percent loss of apatite relative to the initial amount and percent loss of soil phosphorus relative to the initial soil total pool.

Holocene, a result which likely reflects either underestimation of $D_{PCa,0}$, or overestimation of the P flux to the lake. The two measured P values for the granite of the Sargent Mount Pond catchment are very low compared with average granite, and may possibly under-represent the average condition. A curve based on average granite P concentrations [Krauskopf, 1982] implies a loss of 40% by the end of the Holocene, a value that should be regarded as a minimum estimate.

[18] To simulate this loss of apatite P to runoff, we introduce a leakage parameter, α , representing the fraction of P_{Ca} dissolution that is immediately exported from the soil. To find values for α , we calculate the percentage soil P loss curves (equation (2)) and fit equation (4) to these. The value of k is taken from the apatite depletion curves (also shown in Figure 1b), leaving only α to be adjusted:

$$\text{percentage P loss} = 100\alpha(1 - e^{-kt}) \quad (4)$$

[19] The curves provide reasonable fits to the calculated P loss data for both sites. The α values found this way range between 0.3 and 0.9 indicating not only substantial soil leakage rates but also considerable uncertainty.

[20] From the preceding discussion, based on the data presented in Figure 1, two conclusions arise. First, leakage of P from the soils is also substantially greater than the decay rate for available P (an upper limiting estimate for the leakage rate) suggested by Porder *et al.* [2007]. Second, the soil P leakage covaries with the inferred soil apatite concentration, suggesting that the soils only partially capture the P released by apatite weathering. This picture of rapid P leakage appears at odds with the soil chronosequence evidence. We now look more closely at this.

3.2. Re-evaluating Chronosequence Data in Long-Term Soil P Modeling

[21] Here we evaluate the data from four published soil chronosequence studies, Hawaii, USA [Crews *et al.*, 1995; Hedin *et al.*, 2003], and Franz Josef, Reefton, and Manawatu in New Zealand [Walker and Syers, 1976], to see whether the discrepancy can be reconciled. The Hawaii and Franz Josef data sets are identical to those investigated by Porder *et al.* [2007], though our treatment of these is different, particularly in our direct assessment of both apatite depletion and loss of the soil P pool. We treat the chronosequence data exactly as we have treated the lake sediment records, determining rate coefficients for the P depletion. The data for both apatite and total P concentration (Figure 2a) produce curves that are very similar to the lake records, though in some cases covering a very much longer time period. Again, exponential curves have been fitted to the apatite concentrations, the best fit first order decay coefficients ranging from $\log k = -3.4$ at Manawatu to $\log k = -3.8$ at Reefton, values that bracket our results for the two lake sediment records. Our value at Franz Josef is similar to that found by Porder *et al.* [2007] ($\log k = -3.5$). Differences between sites are likely impacted by climate or other factors, but because of the small sample size, this has not been explored.

[22] The percent loss of apatite (Figure 2b), calculated directly from the published data, follows a saturation exponential form just as for the lake sediment records. Ninety percent loss is reached at 6 ka (Franz Josef) and 15 ka (Reefton), bracketing the values for the lake sediment data. Loss of P from the soil, calculated from the declining soil P pool (D_{PT}), follows a similar shape to the apatite loss curve and, just as for the lake

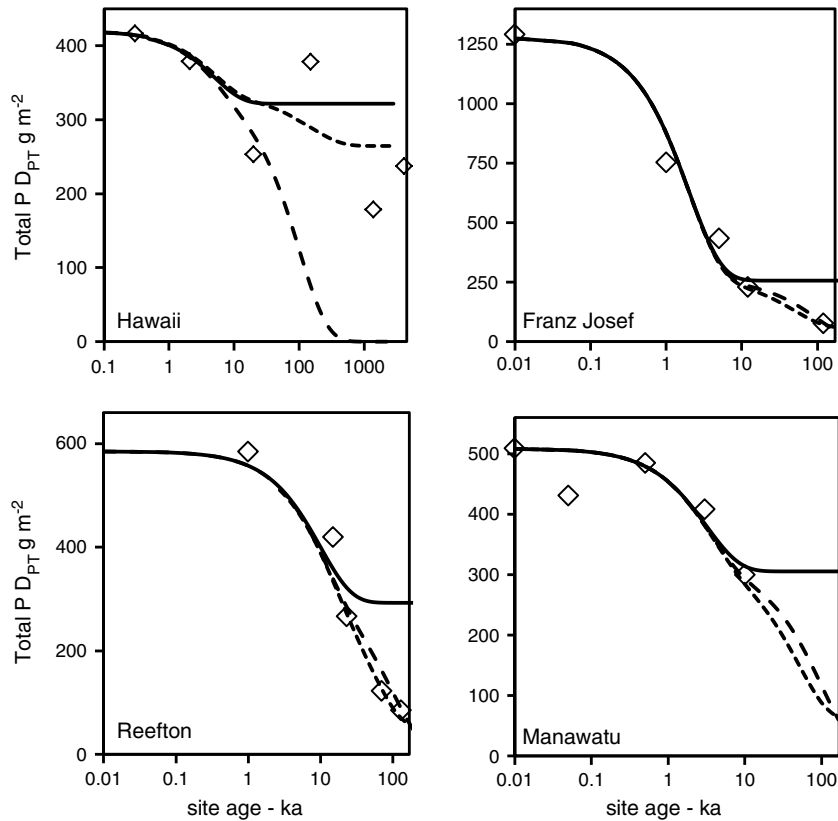


Figure 3. Long-term model fit under three conditions. Leakage of P from apatite, but with no breakdown of secondary soil P and no atmospheric input (solid line). The fit to the observed values (diamonds) is increasingly poor after approximately 10 ka. Leakage also from secondary P (long dash). A good fit is found for all sites except Hawaii. Inclusion of an atmospheric P flux (short dash) improves the fit at Hawaii.

sediment records, can be predicted from the apatite loss curve using the leakage coefficient, α . The shape of the predicted loss curves is, in all cases, similar to the observed data. The best fit values for α , ranging between 0.23 (Hawaii) and 0.9 (Franz Josef), bracket the estimates from the lake sediment records. It should be noted that the high α value at the Franz Josef Glacier site is due to an exceptionally high P content in the youngest soil. If this value is disregarded (Figure 2b, Franz Josef, dashed line), then a much lower α value of just 0.37 is obtained.

[23] Thus far, the lake sediment and soil chronosequence data tell us the same thing. However, we have neglected to consider the release of secondary soil P, a process inherent in the Walker and Syers [1976] conceptual model and addressed in detail by Porder *et al.* [2007]. The possible impact of secondary soil P decay can be tested using the approach of Porder *et al.* [2007] by exploring the extent to which a decay parameter (λ) allows us to better explain the observed data. Equation (5), by predicting changes in soil secondary P density (D_{PS}) through time, allows us to predict the variation in soil total P density (D_{PT} , where $D_{PT} = D_{PCa} + D_{PS}$):

$$\frac{dD_{PS}}{dt} = \lambda D_{PS} + (1 - \alpha)(Q_{atm} + kD_{PCa,0}e^{-kt}) \quad (5)$$

[24] In the relatively short time intervals represented by the data in Figure 2, reasonable values for λ make little difference to the curve shapes. However, if we apply the model to the older soil chronosequence sites (Figure 3), the model fit

becomes increasingly poor after approximately 10^4 years if λ is set at zero. For all sites except Hawaii, this can be solved simply by giving λ a value of $1.0 \times 10^{-5} \text{ a}^{-1}$. To improve the fit for Hawaii, it is necessary to include atmospheric P supply in the model, a flux known to be substantial. Thus, using an atmospheric deposition rate of $0.001 \text{ g P m}^{-2} \text{ a}^{-1}$ for Hawaii [Chadwick *et al.*, 1999] and the other chronosequence sites [Mahowald *et al.*, 2008], we get a far better fit for Hawaii and similar degree of fit at the three younger sites, though the value of λ must be raised to 2.0×10^{-5} . After we have incorporated both atmospheric supply and loss of secondary P into the model, it is no longer possible to use degree of fit for parameterization; higher atmospheric flux values can be made to fit by selecting higher λ values. At Hawaii, the fit shown uses $0.002 \text{ g m}^{-2} \text{ a}^{-1}$ [Hedin *et al.*, 2003] and $\lambda = 6.0 \times 10^{-6}$, but no reliability should be placed on these parameter values; instead, the analysis serves to show two important things. First, for very ancient noneroding soils, interpretation depends critically on the chosen dust flux value, something which will always be poorly constrained for the distant past and is known to vary by orders of magnitude in the Northern Hemisphere through glacial cycles [Mcgee *et al.*, 2010]. Second, at reasonable values for the dust flux, the decay coefficient for secondary soil P is very low, suggesting that this process contributes little to total soil P leakage for soils younger than 10^4 years. Though low in value, this decay constant is very important in long-term modeling; if λ is set at zero for the Hawaii chronosequence, then by 4 Ma, the soils would contain an

Table 3. Study Site Parameters and Environmental Properties

	Log k	α	λ	Mean Annual Precipitation	Setting	Parent Geology
				(m yr^{-1})		
Kråknes ^a	-3.69	≥ 0.45		1.28	Till	Granitic gneiss/amphibolite/schist
Sargent Mountain Pond ^b	-3.62	≥ 0.30		1.4	Till	Granite
Hawaii ^c	-3.62	0.23	6×10^{-6}	2.5	Tephra/lava	Basalt
Franz Josef ^d	-3.52	≥ 0.37	2×10^{-5}	5.09	Glacial outwash	Greywacke & schist
Reefton ^d	-3.77	0.50	2×10^{-5}	2.03	Alluvium	Granite & greywacke
Manawatu ^d	-3.41	0.40	2×10^{-5}	0.85	Coastal dunes	Greywacke

^a*Birks and Wright* [2000].^b*Perry* [2007].^c*Crews et al.* [1995].^d*Walker and Syers* [1976].

additional 4000 g P m^{-2} , or some 10 times the initial soil content at even the lower of the two atmospheric flux estimates.

3.3. A Leaky Model of Long-Term Soil P Dynamics

[25] The parameters identified from the preceding analysis of lake sediment records and soil chronosequence data can be used to quantify a model of long-term soil P dynamics, similar to *Porder et al.* [2007] but including an apatite dissolution leakage term. Good agreement between the lake sediments and the soil chronosequences for the rate of soil apatite loss, and the relatively restricted range in best fit parameter values across a wide range of climates and soil types, suggests that the model can be applied in a generalized way at least in broadly temperate regions. There is no consistent association between parameter values and either climate or geology (Table 3). We must, however, expect that rates would be lower at more arid locations [*Selmants and Hart*, 2010] and also where soils are frozen for much of the year.

[26] The basic premise of the model is that for a newly formed land surface, P is made available to the soil through dissolution of primary apatite and from any atmospheric inputs. The supply of P (Q_{supply}) to the available (including dissolved) soil pool can be expressed in terms of the atmospheric deposition (Q_{atm}) and partial dissolution of primary soil apatite P (D_{PCa}):

$$Q_{\text{supply}} = Q_{\text{atm}} + kD_{\text{PCa}} \quad (6)$$

[27] Whether the atmospheric supply is largely apatite or more available P forms is unimportant owing to the rapid rate of apatite dissolution relative to the timescales at which dust fluxes greatly contribute. Less soluble phases such as monazite are neglected.

[28] The P made available in this way is partially retained in the soil as secondary phases and partially exported to runoff. Slow decay of the secondary soil P contributes to the export and depletes the secondary P pool, the leakage flux (Q_{leakage}) being given by

$$Q_{\text{leakage}} = \alpha Q_{\text{supply}} + \lambda D_{\text{PS}} \quad (7)$$

[29] These expressions fully describe the long-term dynamics for noneroding sites. In the short term, for time periods less than approximately 10^4 years, both Q_{atm} and the decay of D_{PS} are very minor, and export of P to runoff is well described by $\alpha k D_{\text{PCa}}$, a simple fraction of the apatite dissolution rate.

[30] To apply this model in a generalized way, it is necessary to find global values for k , α , $D_{\text{PCa},0}$ (D_{PCa} at time = 0), and for longer time periods, λ and Q_{atm} . For the first three of these, we propose using the mean values for our six sites, yielding $\log k = -3.61$, $\alpha = 0.40$, and $D_{\text{PCa},0} = 540 \text{ g m}^{-2}$, and for λ , we suggest a value of 2.0×10^{-5} . However, the atmospheric flux cannot be generalized in this way owing to its great geographic and temporal variability. Values taken from *Mahowald et al.* [2008] provide a starting point.

3.4. Phosphorus Leakage, Atmospheric Supply, and the Geological Dose Concept

[31] Our analysis suggests that P leaks from soil far more rapidly than has been proposed in other recent studies [*Porder and Hilley*, 2011; *Porder et al.*, 2007]. This difference in interpretation arises partly from our inclusion of an apatite P leakage term and partly from our very much higher estimate for λ , differences that require justification if our findings are to be accepted. In the case of λ , *Porder and Hilley* [2011] find a value of $2.9 \times 10^{-7} \text{ a}^{-1}$, 2 orders of magnitude lower than our estimate, obtained in part from the same data. We attribute this to the way in which the atmospheric flux is treated; if we set the atmospheric flux at zero, then we too get a very low best fit value for λ . Two observations give us confidence that our estimate is approximately correct. First, all four soil chronosequences yield best fit values of the same order for λ ($6 \times 10^{-6} \text{ a}^{-1}$ for Hawaii and $2 \times 10^{-5} \text{ a}^{-1}$ for the other sites). Second, the lysimeter data of *Hedin et al.* [2003] and the soil data of *Crews et al.* [1995] give us a direct estimate for λ of $0.8\text{--}0.9 \times 10^{-5} \text{ a}^{-1}$, essentially identical to our values but 30 times that of *Porder et al.* [2007]. Furthermore, if we use stream water P budget data as an alternative source of information, we also find values close to our estimate. For example, using the P budget at the Hubbard Brook Experimental Forest [*Yanai*, 1992], we obtain a value of $2.2 \times 10^{-5} \text{ a}^{-1}$ (likely an overestimate as a consequence of acidification over the last 100 years [*Reinhardt et al.*, 2004; *Roy et al.*, 1999]). The global runoff and soil data of *Ruttenberg* [2003] (for pre-modern values) yield a value of $0.94 \times 10^{-5} \text{ a}^{-1}$ (range $0.5\text{--}1.9 \times 10^{-5} \text{ a}^{-1}$).

[32] Of potentially greater significance is the observation that P leaks very rapidly from a soil during its early development. How reliable is this? In fact the existence of such leakage is well established and has long been attributed to poor retention of apatite P [*Walker and Syers*, 1976]. It is clearly seen in declining total soil P content in chronosequences [*Crews et al.*, 1995; *Walker and Syers*, 1976], lake sediment

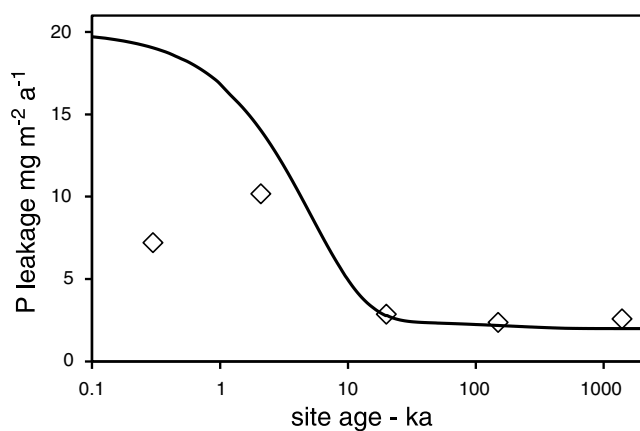


Figure 4. Observed (diamonds; lysimeter data of *Hedin et al.* [2003]) and predicted (line) phosphorus leakage rates at the Hawaii chronosequence. The lysimeters are thought to have underestimated the true rates.

records [*Filippelli and Souch*, 1999], and ecosystem soil budget calculations [*Kařna and Kopáček*, 2006; *Yanai*, 1992]. Direct evidence for leakage from the soil, if not to runoff, and one that allows a simple test of our model output, is provided by the lysimeter data of *Hedin et al.* [2003]. This shows 6–8 mg P m⁻² a⁻¹ of export for the two youngest sites (Figure 4), or about one third of our predicted value. The discrepancy in reality may be smaller than this as the lysimeters, which measured only the filterable dissolved P, yielded flux values lower than in the associated stream water by a factor of >2 (older site only as the two youngest surfaces had no streams) [*Hedin et al.*, 2003]. Consequently, we are confident that P does indeed leach rapidly during early soil development.

[33] A high soil P leakage rate throughout soil development has important implications for our understanding of long-term ecosystem P dynamics. For example, global modeling by *Porder and Hilley* [2011] shows that with a λ value of $0.29 \times 10^{-5} \text{ a}^{-1}$, slightly less than our best estimate value, the initial geological P dose gives way to atmospheric supply as the main predictor of soil P status. The powerful

effect of differences in atmospheric supply is illustrated in Figure 5. At atmospheric flux values below $5 \text{ mg P m}^{-2} \text{ a}^{-1}$ the total P curve shapes are recognizable as the generalized *Walker and Syers* [1976] conceptual model. However, at higher atmospheric deposition rates such as might be expected in southern Europe or during glacial periods, the shapes are wholly different, with increases in the soil total P pool through time heading toward a high steady state after approximately 10^5 years. The relative importance of atmospheric supply increases rapidly through time as the bedrock inheritance is lost (Figure 5b), and at even the lowest atmospheric flux values, atmospheric supply dominates after approximately 10^4 – 10^5 years.

[34] Our analysis therefore opposes the orthodox view that parent bedrock dominates P in soils, such that complete depletion of the geological dose occurs only on rare ancient soils [*Ruttenberg*, 2003]. Furthermore, it follows that this late stage in soil P development, during which atmospheric P feeds the ecosystem, though functionally similar to a “terminal steady state” is conceptually different in as far as it should not be seen as terminal. Indeed, except following glaciations or volcanic activity, or in rapidly eroding landscapes, it is the normal state in which soils are found. In short, the “atmospheric stage” is the norm, and geological dominance is found only in soils on the youngest surfaces ($\ll 10^5$ years), or in regions with erosion greater than 0.02 mm yr^{-1} [*Porder and Hilley*, 2011].

3.5. Ecological Implications of Rapid Soil P Leakage

[35] *Hedin et al.* [2003], based on their analysis of the Hawaii soil chronosequence and lysimeter data, conclude that the export of inorganic P forms is subject to traditional mechanisms of biotic retention. Specifically, they conclude that high P export rates during the early development of the soil are due to N limitation and that declining rates during later development are due to enhanced biotic retention. Our analysis offers an alternative interpretation. In the absence of systematic variations in either the dissolution or leakage coefficients for apatite across the soil chronosequences and lake sediment records, there is no sign of biotic regulation of leakage during early soil development. In the longer term,

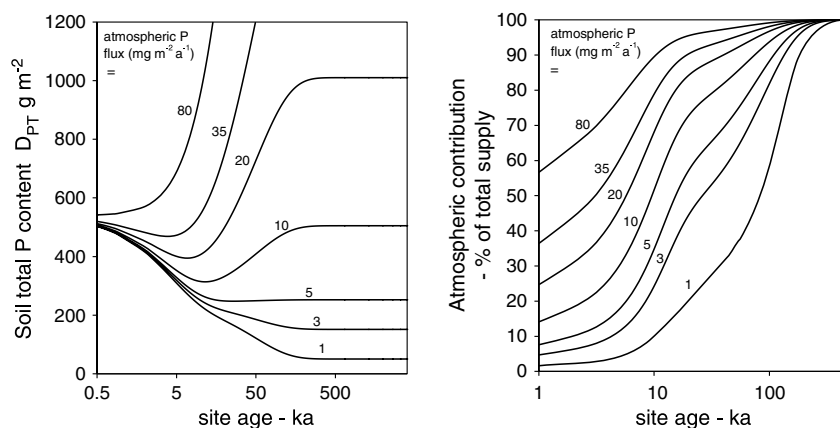


Figure 5. Effect of differing atmospheric P flux on long-term P dynamics. (a) At low atmospheric P supply rates, the curves resemble the Walker and Syers conceptual model. At higher rates, the soil total P climbs to a high steady state. (b) At even the lowest atmospheric P supply rate, total supply from the atmosphere exceeds the initial geological supply within 10^5 years.

during the atmosphere-dominated stage on older soils in Hawaii, where ecosystem productivity is P limited, total P loss from soil is equal to the atmospheric flux [Hedin *et al.*, 2003] and is thus independent of the state of P limitation. This suggests that whatever the role of biotic mechanisms in regulating the availability of P to plants, soil P leakage throughout soil development appears to be regulated primarily by physical rather than biological constraints.

[36] In the very short term, annual P uptake requirement of an ecosystem is largely supplied by biological recycling [Chapin *et al.*, 1978; Yanai, 1992], and even during the earliest stage of soil development, the flux of newly released P from apatite dissolution is minor compared with the annual P uptake of $960 \text{ mg m}^{-2} \text{ a}^{-1}$ [Yanai, 1992] at Hubbard Brook. Our high leakage rate of apatite P does not therefore challenge the accepted view that ecosystem P availability will increase through the early stages of soil development as the soil pool of available P grows [Walker and Syers, 1976]. However, the higher P leakage rates we propose will lead to control of soil P supply by atmospheric deposition, at soil chronosequence sites or other noneroding settings, much sooner than suggested by Crews *et al.* [1995] and subsequent studies in Hawaii. At sites where the atmospheric contribution is small, our results agree with the view of Walker and Syers [1976] that available secondary P concentrations will start to significantly decline after the primary apatite is depleted. That this also leads to P limitation of ecosystem productivity is demonstrably the case at the Franz Josef [Richardson *et al.*, 2004] and Hawaii [Hedin *et al.*, 2003] chronosequences.

[37] Whatever its impact on terrestrial ecosystems, rapid leakage of soil P from newly formed land surfaces will profoundly impact the ecology of upland streams and lakes, systems that derive most of their water from shallow flow paths. Immediately after exposure of the new land, surface water P concentrations will be very high. Indeed, the P flux curves of Figure 1 suggest a peak runoff concentration for total P (allowing for lake retention and focusing effects) in the order of $100 \mu\text{g L}^{-1}$ at 10–11 ka, falling to $15 \mu\text{g L}^{-1}$ prior to modern disturbance. These lakes, and others on deglaciated land, should have been most productive in the early post-glacial. Paleocological evidence at Kråkenes Lake is consistent with this interpretation; productivity increased at the start of the Holocene, before declining after 10.7–10.8 ka ([Birks *et al.*, 2000]. At Sargent Mountain Pond, paleoproductivity has not been examined at high resolution but diatom assemblages prior to the Holocene are consistent with a pH close to 8 and high P availability [Norton *et al.*, 2011]; diatom analysis of other sites in Britain [Haworth, 1969], Sweden [Digerfeldt, 1972, 1975], and Finland [Sarmaja-Korjonen *et al.*, 2006] also shows an oligotrophication through the early Holocene.

[38] The early post-glacial high P supply rate to these lakes also implies a high rate of supply to coastal ecosystems. To consider the possible magnitude of this effect, let us suppose that all deglaciated land experienced an enhanced release of P to runoff of $42 \text{ mg P m}^{-2} \text{ a}^{-1}$ (mean initial rate calculated for our six sites) at the start of the Holocene. Then the $18 \times 10^6 \text{ km}^2$ would supply $8 \times 10^{11} \text{ g a}^{-1}$ of additional P, or 4% of the current total estimated riverine supply to the oceans [Ruttenberg, 2003]. Could this be sufficient to drive the long-term ocean core P cycles identified by Filippelli *et al.* [2007]? Given the long residence time of P in the oceans, and the relatively short-lived nature of this P pulse,

it seems unlikely there would be a detectable global impact. However, most of riverine P is delivered in low latitudes; if we repeat the calculation at high latitudes, then a far greater effect is expected. This situation is probably best represented by the Baltic Sea due to its high degree of isolation from the open ocean and exceptionally large proportion of land deglaciated since the Last Glacial Maximum. Could the early Holocene episode of hypoxia in the Baltic [Zillén *et al.*, 2008] be a response to a transient P supply surge?

4. Conclusion

[39] Our analysis of new and existing lake sediment and soil chronosequence data yields a coherent picture of long-term soil P dynamics at noneroding sites that differs markedly from the prevailing view. This is particularly important in three aspects.

[40] First, it is clear that P leaks from soil profiles far more rapidly than is generally thought, with the consequence that relative to any inherited geological dose, the atmospheric delivery of P is of far greater importance in the long term. The “terminal steady state” stage in soil development, when any P inherited from the bedrock and surficial material has been depleted, will typically be reached after some 10^4 to 10^5 years, and must be regarded as the norm outside areas of recent glaciation or other disturbances, rather than the rare exception.

[41] Second, particularly rapid leakage of P from soils during their early development greatly limits the scope for terrestrial ecosystems to self-regulate the leakage of P from soil. Taken together with the observation that during the atmospheric stage, leakage must also be physically not biologically constrained, we conclude that loss of P from soil profiles owes little to biotic retention.

[42] Third, leakage of P during the early apatite rich stage of a soil’s development means that in young landscapes, streams and lakes fed by soil water experience high P loadings, a matter of profound significance for the interpretation of post-glacial ecosystems.

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