

The role of rock weathering in the phosphorus budget of terrestrial watersheds

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Accepted 4 May 1990

Key words: phosphorus, stream chemistry, weathering

Abstract. Residual soils (saprolites) developed on crystalline rocks appear to form by an essentially isovolumetric process (i.e. without dilation or compaction). Isovolumetric geochemical analysis of a suite of saprolite samples developed on a common parent rock can be used to estimate the relative rates of long-term losses of P and Si during weathering. Using the export of dissolved Si in rivers as a weathering index, one can then estimate the rate of P release due to chemical weathering by means of the P–Si loss ratio in saprolite. For three basins where data are available (Liberty Hill, SC; Amazon River, Brazil; Rio Negro, Brazil) estimated P weathering release rates are 163, 457, and 242 moles P km⁻² yr⁻¹, respectively. These compare to precipitation inputs of 684, 700 and 630 moles P km⁻² yr⁻¹ and total river exports of 256, 4490 and 820 moles P km⁻² yr⁻¹, respectively. The Rio Negro shows a near perfect balance between the input of P via precipitation and chemical weathering and the riverine output of dissolved and suspended P. This system, however, raised the unsolved problem of the source that supports the atmospheric P input.

Introduction

The mobilization of phosphorus by rock weathering is of interest to soil scientists and ecologists because of the role of P in the productivity of terrestrial and aquatic ecosystems. Despite the importance of chemical weathering to the biogeochemical cycle of phosphorus, there appear to be few data pertaining to this subject. Garrels et al. (1975: 105) state that on a global scale weathering releases 5.5×10^{10} moles of P per year but do not cite any references to support this figure. Meybeck (1982) assumed an input of 25×10^{10} moles P yr⁻¹ to the global soil phosphorus reservoir via rock weathering in order to balance outputs from this reservoir. Olsson and Melkerad (1989) calculated a long-term release of P by weathering of glacial till in southern Sweden at a rate of 280 moles P km⁻² yr⁻¹. This was based on a comparison of the P content of fresh and weathered till and the assumption that Ti has been conserved during weathering since deglaciation. However, as I have noted in an earlier paper (Gardner 1980), the assumption of Ti conservation during weathering is suspect.

Some workers have used the discharge of dissolved silica as an index of the release of dissolved P from rocks by weathering (Lewis et al. 1987). These workers assume that dissolved P and Si are released from weathering rocks in the same proportion as their mole ratio in the fresh rock (i.e. the rock dissolves

congruently). On this basis, Lewis et al. (1987) calculated a weathering release rate of 1,015 moles dissolved P km⁻² yr⁻¹ for the Caura River basin in Venezuela as compared to a measured discharge of 750 moles dissolved P km⁻² yr⁻¹ and 720 moles suspended P km⁻² yr⁻¹. This discrepancy between the calculated and measured export of dissolved P suggests that this method may overestimate the rate of P release by chemical weathering because,

- some of the P in the fresh rock is occluded as tiny crystals of unleachable apatite in resistant minerals such as quartz,
- the soil solution becomes saturated with respect to primary P minerals (but not primary silicates) thereby preventing further dissolution, or some of the released P is precipitated as secondary P minerals or is adsorbed on secondary clays.

In a study of four New Zealand soils, Walker and Syers (1976) reported long-term rates of P loss of 1,606, 600, 600 and 0.0 moles P km⁻² yr⁻¹ as compared to an average atmospheric input of about 310 mole P km⁻² yr⁻¹. These estimates, however, are based on studies of the upper soil profile and do not take into account the possible retention of some of the mobilized P lower in the profiles. Some of the atmospheric P input may be converted to organic phosphorus in the upper part of the profile so that actual releases by weathering may be higher than those listed above.

The most direct method of approaching this problem would be to measure the concentration of dissolved P in waters draining from soil profiles. Aside from the difficulty of sampling such water, there might be problems in interpreting the results because some of the phosphorus could be derived from sources other than rock weathering, such as atmospheric inputs, fertilizer and organic matter decomposition. Phosphorus leached from the rock might also precipitate or adsorb on secondary minerals.

In view of these difficulties, the purpose of this paper is to suggest an alternative method for evaluating the mobility of P during weathering and to discuss the role of weathering in the P budget of terrestrial watersheds. This method can be applied to residual soils formed on crystalline rocks that retain the original textural and structural features of the parent rock. Such soils commonly are called saprolites and can be assumed to have formed in an isovolumetric fashion (Millot & Bonifas 1955) such that a unit volume of soil can be considered to have evolved from an equal volume of fresh rock without experiencing dilation or compaction (Gardner 1980; Gardner et al. 1978). Accordingly, if bulk density measurements are available, chemical analyses of soil samples can be converted from a mass percent basis to a mass per unit volume basis so that estimates of the absolute losses (or gains) of elements during weathering can be made (Gardner 1980; Gardner et al. 1978). Furthermore, because rock textures are only preserved in soils below the zone of root penetration, plant uptake below this depth should be nonexistent and thus any changes in the volumetric P concentration can be attributed solely to weathering.

By analyzing a suite of saprolite samples from a profile developed on a

uniform parent rock, one can establish an empirical reaction-progress relationship between the isovolumetric concentration of P_2O_5 (in $g\text{ cm}^{-3}$) and bulk density (which is an overall index of weathering). Such relationships can also be established for other rock constituents (SiO_2 etc.). The ratio of the slope of P_2O_5 ($g\text{ cm}^{-3}$) versus bulk density ($g\text{ cm}^{-3}$) to the slope of some other reference element versus bulk density can be taken as the long-term average of the relative rates of loss of P_2O_5 and the reference element from the rock due to weathering. For this purpose, SiO_2 is probably the best reference element because of its negligible atmospheric input (Johnson et al. 1981; Bricker et al. 1983; Lewis et al. 1987) and its limited biological uptake. As the export of dissolved SiO_2 from a watershed can be determined from measurements of stream chemistry and discharge, an estimate of the rate of phosphorus release by weathering can be obtained by multiplying the SiO_2 export rate by the ratio of the slopes of the P_2O_5 and SiO_2 versus bulk density trends from the saprolite data.

The isovolumetric assumption

Because the method and results presented below are based on the assumption that saprolite formation is essentially isovolumetric, a brief justification of this assumption is given here. The isovolumetric assumption is based primarily on the close visual similarity of the textures and structures in saprolite to those in the parent rock. Although this assumption cannot be proved in a rigorous fashion (at least not without an exhaustive petrographic study), there are, in addition to the textural similarity, several other lines of evidence supporting this assumption (Gardner 1980). First, in most weathering reactions involving silicates the molar volume of solid reactants exceeds that of solid products, even when aluminum is conserved. Second, delicate, undeformed, needle-like clays in saprolite (Keller 1977) preclude substantial compaction. It is also unlikely that growth of delicate clays could have exerted expansive forces on the saprolite matrix. Third, expansion during pedogenesis seems to occur in soils such as caliches where accumulating secondary $CaCO_3$ (or other cements) must be accommodated in a limited amount of original void space and leads to an increase in bulk density (Gardner 1972). Saprolite formation, on the other hand, involves intense leaching, mass loss and void space creation and thus is not likely to generate expansive forces in excess of the confining pressure of the overburden. Fourth, orthogonal joint systems in saprolite show no deformation as might be expected if the soil volumes bounded by the joints (which vary in bulk density) had expanded or compacted differentially (for example see photo on p. 48 in Gilluly et al. 1968). Finally, it should be noted that the loss ratios of P_2O_5 to SiO_2 computed below are insensitive to compaction because in any individual sample the volumetric concentrations of P_2O_5 and SiO_2 would be subject to the same compaction correction factor (a number less than 1.0). The loss ratio would only be in error if P is in fact immobile and expansion has been great enough to produce an apparent, rather than real, loss. This is unlikely for the

profiles described below because application of an expansion correction factor (a number greater than 1.0) large enough to make P immobile (i.e. slope = 0.0) would result, in most cases, in apparent gains of constituents such as SiO₂ and K₂O.

Sources of data

Evaluation of element mobility by means of the isovolumetric technique requires the collection and analysis of a suite of saprolite samples derived from a common parent rock (Gardner et al. 1978). Ideally the suite should cover the widest possible range of bulk density from fresh rock to the most highly weathered material that still retains the texture of the parent rock. In order to establish whether there is a trend of decreasing isovolumetric concentration of an element with decreasing bulk density, the number of samples in the suite should probably exceed five and should be more or less evenly spaced over the range in bulk density. Unfortunately relatively few geochemical studies of residual soils have been conducted with the purpose of isovolumetric interpretation in mind and thus do not contain measurements of bulk density.

Some of the data on which this paper is based were published by C. V. Clemency (1977). He collected and analyzed a large number of saprolite suite developed on a variety of igneous and metamorphic rocks in southern Brazil. At my request, Professor Clemency (pers. comm.) has graciously identified those of the published suites that in his judgement probably evolved in an isovolumetric fashion. In addition, I have analyzed 11 saprolite suites from the crystalline rocks of the South Carolina Piedmont. Also included in this study are two andesite saprolite suites from California (Hendricks & Whittig 1968). Each set of data from these sources includes measurements of dry mass (110°C), bulk density, and the concentrations of the major rock forming oxides.

Analytical methods

Samples from Brazil were analyzed by rapid wet-chemical methods (Sharpiro 1975; Clemency 1977). Samples from South Carolina were analyzed by X-ray fluorescence spectrometry using pressed powders and a two-stage calibration procedure (Holland & Brindle 1966; Gardner in press). XRF calibration employed a Lucas-Tooth, Pyne (LTP) model (Lucas-Tooth & Pyne 1964) and was based on 55 natural and synthetic standards covering a wide range of composition. Correlation coefficients for the P₂O₅ and SiO₂ calibrations were 0.9984 and 0.9974, respectively. The root mean square error (RMSE) for the P₂O₅ and SiO₂ calibrations were 0.031% and 1.25%. The mean relative errors of calibration (100% RMSE/mean concentration of analyte in standards) were 11.7% (P₂O₅) and 2.50% (SiO₂).

Results

An example plot of the isovolumetric concentrations of P₂O₅ and SiO₂ versus

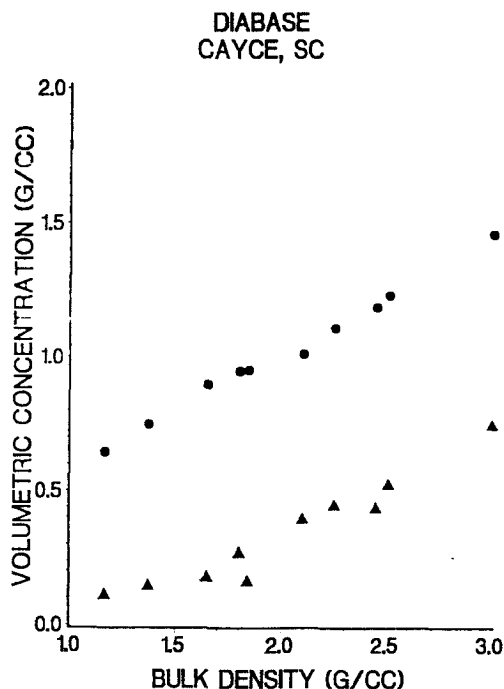


Fig. 1. Volumetric concentrations of SiO₂ (circles) and P₂O₅ (triangles) versus bulk density for the Cayce, SC diabase saprolite. P₂O₅ concentrations multiplied by 100.

bulk density is shown on Fig. 1. Linear regression analyses of the volumetric concentration versus bulk density data are summarized in Table 1. Of the 26 available suites, nineteen show statistically significant slopes for the P₂O₅ versus bulk density regression.

In three of the Brazilian suites that have nonsignificant slopes (Perus granite, Curitiba rhyolite and Pocos de Caldas syenite), the concentration of P₂O₅ in the fresh rock is on the order of 0.01 to 0.02 mass percent which is near the limit of detection for the wet chemical method used by Clemency (1977). Other suites that have low levels of P₂O₅ in the fresh rock are the Edgefield (SC) granite, the Table Rock gneiss and the Kings Creek sericite. These suites also have non-significant regression slopes and/or low R² values. Thus more sensitive and precise methods of P analyses may be required to determine whether or not phosphorous is actually conserved during the weathering of these suites.

In all cases SiO₂ shows a distinct linear decrease in isovolumetric concentration with decreasing bulk density. Table 2 shows the weight and molar loss ratios of P to Si based on regression slopes in Table 1. The average molar ratio for the Brazilian suites is 0.00295, whereas that for the South Carolina suites (with the unusual high P Enoree vermiculite excluded) is 0.00124.

Table 1. Linear regression analysis of SiO₂ versus bulk density and P₂O₅ versus bulk density for saprolites.

Profile	SiO ₂			P ₂ O ₅			
	Int.	Slope	R ²	Int.	Slope	R ²	
		Brazil					
Amphibolite	-0.05	0.590	.979	-0.00002	0.00240	.869	
Amphibole Schist, Alts Serra	-0.13	0.683	.995	-0.0146	0.00762	.983	
Basalt, Jupia	-0.21	0.567	.995	-0.0055	0.00404	.824	
Fenite, Pocos de Caldas	-0.13	0.615	.980	-0.0197	0.02052	.879	
Granite, Perus	-0.11	0.768	.989	-0.00073	0.00069*	.461	
Granite (A), Sorocaba	-0.33	0.816	.968	-0.01300	0.00713*	.638	
Granite (B), Sorocaba	-0.13	0.745	.982	-0.00769	0.00476	.740	
Granite, Ubatuba	-0.025	0.743	.974	-0.00329	0.00324	.640	
Granite, Sao Roque	-0.03	0.688	.946	-0.0149	0.00803	.954	
Granite, Itapevi	-0.25	0.810	.979	0.00061	0.00052*	.124	
Phonolite, Pocos de Caldas	-0.39	0.737	.992	0.00172	0.00228*	.564	
Rhyolite, Curitiba	-0.11	0.794	.999	0.00005	0.00008*	.126	
Syenite, Pocos de Caldas	-0.49	0.718	.956	-0.00004	0.00017*	.284	
		California					
H. Andesite	-0.25	0.630	.989	-0.0020	0.00210	.960	
O. Andesite	-0.38	0.650	.962	-0.0030	0.00295	.753	
		South Carolina					
Granite, felsic, L.H.**	-0.10	0.757	.996	-0.00220	0.00170	.918	
Granite, mafic, L.H.	-0.04	0.719	.994	-0.00373	0.00252	.720	
Granite, porphyritic, L.H.	-0.09	0.738	.994	-0.00210	0.00166	.719	
Felsic dike, L.H.	0.00	0.692	.999	-0.00200	0.00154	.400	
Granite, Cacye	0.01	0.719	.987	-0.00250	0.00183	.699	
Granite, Edgefield	0.19	0.798	.998	-0.00017	0.00033	.279	
Gneiss, Table Rock	-0.04	0.745	.996	-0.0003	0.00041*	.409	
Sericite, Kings Cr.	-0.17	0.760	.952	-0.00049	0.00045	.190	
Vermiculite, Enoree	-0.05	0.466	.989	-0.05320	0.05156	.794	
Gabbro, Ridgeway	-0.03	0.481	.865	-0.00413	0.00321	.929	
Diabase, Cacye	0.17	0.423	.991	-0.00350	0.00351	.922	

*Slope of regression line not significantly different from zero at 0.05 probability level.

**L.H. = Liberty Hill

Applications

In areas where data are available for stream discharge and chemistry, the ratios shown in Table 2 can be used to estimate the release of phosphorus due to chemical weathering. For example, the Liberty Hill granite underlies two small watersheds that were studied by Kheoruenromne (1976). On the basis of discharge measurements and chemical analyses he estimated that dissolved SiO₂ is exported from the landscape at a rate of 1.47×10^5 moles km⁻² yr⁻¹. Applying an average molar loss ratio of 0.00111 for the four Liberty Hill suites (Table 2), the rate of release of P due to weathering is estimated to be 163 moles km⁻² yr⁻¹. By comparison Kheoruenromne's data indicates that inputs of dissolved and

Table 2. Weight and molar loss ratios of phosphorus to silicon based on regression slopes in Table 1.

Profile	P ₂ O ₅ /SiO ₂ (g/g)	P/Si (mole/mole)
	Brazil	
Amphibolite	0.00407	0.00170
Amphibole schist	0.01116	0.00465
Basalt	0.00713	0.00297
Fenite	0.03337	0.01392
Granite, Perus	0.00090	0.00038
Granite (A), Sorocaba	0.00874	0.00364
Granite (B), Sorocaba	0.00640	0.00267
Granite, Ubatuba	0.00436	0.00182
Granite, Sao Roque	0.01167	0.00487
Granite, Itapevi	0.00064	0.00027
Phonolite	0.00309	0.00129
Rhyolite	0.00010	0.00004
Syenite	0.00024	0.00010
	California	
H. Andesite	0.00333	0.00139
O. Andesite	0.00454	0.00189
	South Carolina	
Granite, felsic	0.00225	0.00094
Granite, mafic	0.00350	0.00146
Granite, porphyritic	0.00225	0.00094
Felsic dike	0.00223	0.00093
Granite, Cacye	0.00255	0.00106
Granite, Edgefield	0.00041	0.00017
Gneiss	0.00055	0.00023
Sericite	0.00059	0.00025
Vermiculite	0.11052	0.04609
Gabbro	0.00667	0.00278
Diabase	0.00830	0.00346

total P via precipitation amount to 273 moles km⁻²yr⁻¹ and 684 moles km⁻²yr⁻¹, respectively, whereas the stream exports of dissolved P and total P amount to 89 moles km⁻²yr⁻¹ and 255 moles km⁻²yr⁻¹. As can be seen the export of dissolved P is equal to about 55 percent of the weathering release based on the P-Si loss ratio. Because the phosphorus released by saprolite formation is largely out of the reach of upland plant roots, this discrepancy indicates that some of the phosphorus released by rock weathering is taken up by aquatic and/or riparian plants in the stream, precipitated and/or adsorbed.

On a larger scale one can use the loss ratios for the Brazillian saprolites in Table 2 to estimate the rate of phosphorus release due to chemical weathering in the Amazon Basin. On the basis of data presented by Oltman (1968) it is estimated that the export of dissolved SiO₂ from the Amazon Basin amounts to about 1.55×10^5 moles km⁻²yr⁻¹. The average molar loss ratio for the 13 Brazillian saprolites in Table 2 is 0.00295. Thus the estimated rate of release of

dissolved P due to weathering in the Amazon basin is about 457 moles $\text{km}^{-2} \text{yr}^{-1}$. Using the data given by Meybeck (1982) for the Amazon River, the export of total dissolved phosphorus (TDP) from the basin is 547 moles $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$ of which 328 moles is in the form of phosphate. The atmospheric loading of dissolved P in the Amazon Basin is about 700 moles $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$ (Meybeck 1982) and again surpasses the rate of release by rock weathering (457 moles $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$).

Applying the same P-Si loss ratio (0.00295) to the Rio Negro basin and using the dissolved SiO_2 ($65 \mu\text{mole l}^{-1}$) and discharge (1.26 m) data of Stallard & Edmonds (1983) and van Bennekon & Salomons (1980), respectively, yields a P weathering release rate of 242 moles $\text{km}^{-2} \text{yr}^{-1}$. This compares to an atmospheric input of 630 moles $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$ (van Bennekon & Salomons 1980) and riverine exports of 380 moles dissolved $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$ (van Bennekon & Salomons 1980) and 500 moles suspended $\text{P} \cdot \text{km}^{-2} \text{yr}^{-1}$ (Gibbs 1967). In the absence of a significant input of primary particulate P by physical erosion of fresh rock in the low-relief basin of the Rio Negro, these results suggest a near-perfect balance between input and export. However, as discussed below, such a result raises the question of the source(s) of P that supports atmospheric deposition.

Discussion

Inferences regarding the role of rock weathering in the cycle of phosphorus should be made with a clear understanding of the limitations of the method proposed in this paper. The formation of saprolite requires the long-term leaching of constituents from the parent rock. For a typical saprolite (10–20 m thick) the amount of time required is probably on the order of one to five million years. Modern environmental conditions of climate, hydrology and vegetation may not be representative of the long-term average conditions which governed the P to Si loss ratio recorded in saprolite. In low-lying tropical areas where climatic fluctuations are probably modest this may not be a severe problem. However, in more temperate areas such as the Piedmont of the southeastern United States, climatic fluctuations probably have been more dramatic, as evidenced by the pollen stratigraphy of lake sediments (Frey 1953; Whitehead 1967). In addition the Piedmont has suffered modest stream incision as a result of base level changes due to mild tectonic warping and glacial lowering of sea level (Colquhoun & Johnson 1968; Colquhoun et al. in press). As a result of the slopes that have developed, the A and B soil horizons overlying the saprolite in many areas of the Piedmont are rather poorly developed in relation to the thickness of the saprolite beneath. The modern soil profile may be developing on a parent material of saprolite rather than fresh rock. The leaching of Si from the saprolite at the base of the soil may be stoichiometrically different in relation to P than that occurring at the interface between fresh rock and saprolite.

In most landscapes the interface between saprolite and fresh rock lies well below the depth of root penetration. As a result, the dissolved P released by rock

weathering is not available to upland plants. Furthermore the P released by rock weathering enters streams largely by way of groundwater seepage and base flow. Upon reaching the riparian zone some of the dissolved P may be taken up by vegetation or may be precipitated or adsorbed. Nevertheless if one wishes to estimate the rate of release of dissolved P by rock weathering using isovolumetric saprolite chemistry, one should base the estimate on the base flow discharge of SiO_2 rather than the total discharge, as is usually done. This alleviates the problem (noted above) posed by the possible difference in P-Si loss stoichiometry between the top of the saprolite and the rock-saprolite interface.

Subsequent to their release from parent rocks, both dissolved P and Si are subject to possible incorporation into solid phases. Of the two, phosphorus is more likely to be removed from solution because of its greater biological activity and affinity for adsorption on clays and iron oxides. However, if Si is removed from stream water, its use as an index for the release of dissolved P by chemical weathering is compromised. This is most likely to occur in large lakes where diatom blooms might remove Si from the water and deposit opal in the lake sediments. Uptake of dissolved phosphorus released by rock weathering is most likely to occur in the riparian zone or in the stream. Such uptake will convert dissolved phosphorus into organic or particulate inorganic forms which may then be exported from the watershed as part of the suspended load.

The major P inputs that are usually considered in the phosphorus budgets for pristine basins are atmospheric deposition and release from rock by chemical and physical weathering. The chief outputs include stream export of dissolved and particulate P and loss of P from the watershed by volatilization and deflation. Typically the atmospheric input of P to a watershed is measured using precipitation collectors. Despite some limitations (Hicks 1980; Lewis 1983), the atmospheric input can be more or less directly measured, at least in principle. Stream exports of dissolved and particulate P are also directly measurable by well established techniques. The remaining components of the P budget can be estimated only on the basis of surrogate measurements and/or assumptions. As noted above, the release of P due to chemical weathering can be estimated using the discharge of dissolved Si as an index and by assuming either congruent dissolution of the parent rock or the P-Si loss ratio based on isovolumetric measurements of saprolite chemistry. Estimation of the rates of input by physical weathering and loss by volatilization and/or deflation pose conceptual and measurement difficulties.

An example of such difficulties is seen for the Caura River, (Venezuela). Lewis et al. (1987) used the riverine export of particulate Si as an index for computing the input of P due to physical weathering in the Caura River basin. This was done by multiplying the discharge of particulate Si by the mass ratio of P to Si in the fresh rock. The input due to physical weathering so computed was $685 \text{ moles P km}^{-2} \text{ yr}^{-1}$, which when added to the estimated input from chemical weathering ($1015 \text{ moles P km}^{-2} \text{ yr}^{-1}$) and the measured atmospheric input

(440 moles P km⁻² yr⁻¹) gives a total input of 2140 moles P km⁻² yr⁻¹. The measured riverine exports of dissolved and suspended P were 750 and 720 moles P km⁻² yr⁻¹, respectively. The difference between input and riverine export (640 moles P km⁻² yr⁻¹) was assumed to be retained by the watershed.

The use of riverine export of particulate Si as an index for computing the input of P due to physical weathering has two problematic assumptions. First this method implicitly assumes that the rate of physical weathering is equal to the rate of mechanical erosion, which may or may not be true. Furthermore, physical weathering by definition is simply the mechanical breakdown of rock into finer sized fragments without any change in bulk chemistry or mineralogy. Thus if it is assumed that all of the riverine particulate Si has been derived solely by physical weathering, then by definition none of the P associated with particulate Si has ever been released to solution and available for biological uptake. In the Caura River 685 of the 720 moles of suspended P would fall into this category. From the ecological point of view particulate P that has been formed by physical weathering and then exported by river discharge has been inert during its residence in the watershed.

Rather than attempting to estimate the rate of physical weathering using riverine particulate Si as an index, it might be more meaningful (and less problematic) to measure the fraction of the riverine particulate P that occurs in the form of organic, adsorbed and newly precipitated P by using selective extraction procedures such as those proposed by Williams et al. (1967). The extractable fraction of particulate P can be assumed to have existed in dissolved form at some point during its residence in the watershed. The mass budget could then be simplified to include inputs due to atmospheric deposition and chemical weathering and outputs due to volatilization, deflation and riverine exports of dissolved and extractable particulate P. This simplified mass budget would be particularly useful in high relief watersheds with erodible soils where the rate of mechanical erosion greatly exceeds chemical denudation and where the export of P in suspended matter may greatly exceed its export in dissolved forms (Graham & Duce 1979). In such cases much of the suspended P may be primary rock phosphorus that has simply been mechanically weathered and eroded.

The assumption that the difference between P input and riverine export is retained in the watershed also is problematic because it fails to question the source of the atmospheric P input. On a continental scale the average rate of atmospheric P input appears to lie between 250 and 750 moles P km⁻² yr⁻¹ (Graham & Duce 1979; Meybeck 1982; Martin & Harr 1988). Continental atmospheric P deposition can not be supported by long distance transport from the oceans because ocean surface waters have a very low concentration of P, especially in comparison to Cl which is the primary indicator of oceanic sources. Thus on a continental scale we must conclude that atmospheric P deposition is supported by volatilization and/or deflation from continental sources (Graham & Duce 1979). It is not known whether the Caura River basin retains the entire difference between P input and riverine P export. To the extent that this is so, the Caura River basin is subsidized by atmospheric transfers of P from other

continental areas. The available measurements (Herrera 1979) of P volatilization from soil (~ 2.0 moles P km⁻² yr⁻¹) are far too low for atmospheric deposition to be supported entirely by local sources. Pollen also could be a local source for atmospheric P deposition but presently available data on pollen deposition (Doskey & Ugoagwu 1989) are too imprecise and site specific to estimate the magnitude of this flux in rainforests. It is possible that rain forests in general are subsidized by P transfers from drier areas where fires and deflation are more common. Lawson & Winchester (1979), however, have found that S, K and P concentrations in aerosol particles are not affected by rainfall events and are not associated with concentrations of soil-derived elements (Al, Si, Ca, Fe), thus suggesting a local but unidentified biogenic origin. If the atmospheric input is supported solely by forest fires and if the inventory of P in forest biomass is on the order of 10^5 to 10^6 moles P km⁻² (Golley 1975), then a given patch of forest would have to burn completely every 200 to 2000 years on average. Whether this in fact occurs is not known at present.

Given the importance of phosphorus as a nutrient element in terrestrial ecosystems, surprisingly little is accurately known about the major components of its budget. Table 3 summarizes our current but meager data for the role of weathering in terrestrial P budgets. If we are to achieve a better understanding of P budgets in terrestrial landscapes, research is needed on several fronts.

- First, we must develop a method for estimating the input of P due to physical weathering and develop an extraction technique for riverine particulate P that will accurately estimate the percentage of particulate P that was at some point in its history in soluble form. This presumably would include adsorbed and organic particulate P and phosphorus that has been trapped in secondary Al and Fe sesquioxides.
- Second, we need a better understanding of the sources and modes of deposition of atmospheric P. This will require study of the morphology, chemistry and mineralogy of atmospheric particulate matter coupled with closely spaced time-series measurements of dry and wet deposition. With such information and supporting meteorological data, it may be possible to identify the source regions of wet and dry deposition.
- Third, we must understand more clearly the mechanisms by which P is removed from the land surface to the atmosphere.

What roles do volatilization from the soil, pollen release, fires and deflation play in the transfer of P from the land to the atmosphere? How do the rates of these processes vary among ecosystems and landscapes? Finally we need to ascertain the fate of soluble P after its release from rock by chemical weathering. I have suggested that much of this P is unavailable to upland vegetation. Is it heavily used by riparian vegetation or is most of it simply exported to the oceans in dissolved and/or adsorbed form? If the latter, chemical weathering of rock may play little role as compared to atmospheric deposition in the biogeochemistry of P in terrestrial environments.

Table 3. Available estimates of rates of P release due to weathering (moles P km⁻² yr⁻¹). Estimates are for chemical weathering except where noted.

Area	Estimate	Method	Source
Global	95	Not given	Garrels et al. (1975)
Global	430	Assumed for balance	Meybeck (1982)
Southern Sweden	280	Soil chemistry Ti assumed conserved	Olsson & Melkenrud 1989
Caura R. Basin Venezuela	1015	Dissolved Si index, congruent rock dissolution	Lewis et al. (1987)
Caura R. Basin	685*	Suspended Si index, congruent rock dissolution	Lewis et al. (1987)
New Zealand (Franz Josef)	1600	Soil profile chemistry, estimated soil age	Walker & Syers (1976)
New Zealand (Reefton)	600	Soil profile chemistry, estimated soil age	Walker & Syers (1976)
New Zealand (Marawater)	600	Soil profile chemistry, estimated soil age	Walker & Syers (1976)
New Zealand (Canterbury)	0	Soil profile chemistry, estimated soil age	Walker & Syers (1976)
Liberty Hill, SC	163	Dissolved Si index, isolvolumetric saprolite chemistry	This paper
Amazon Basin	457	Dissolved Si index, isolvolumetric saprolite chemistry	This paper
Rio Negro Basin	242	Dissolved Si index, isolvolumetric saprolite chemistry	This paper

* Estimate of P release due to physical weathering. See text for discussion.

Acknowledgements

I wish to thank Dr. Charles V. Clemency (SUNY, Buffalo) for generously sharing his Brazillian saprolite data with me. Dr. Thomas Williams reviewed an early draft of the manuscript. Drs. William Lewis, William Schlesinger and an

anonymous reviewer also provided numerous helpful suggestions. Dr. John Shervais and Mr. Marion Rushing assisted with the XRF analyses. Mrs. Jean Rembert graciously typed the manuscript.

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