

# **The Global Phosphorus Cycle**

Introduction

The Pools and the Fluxes

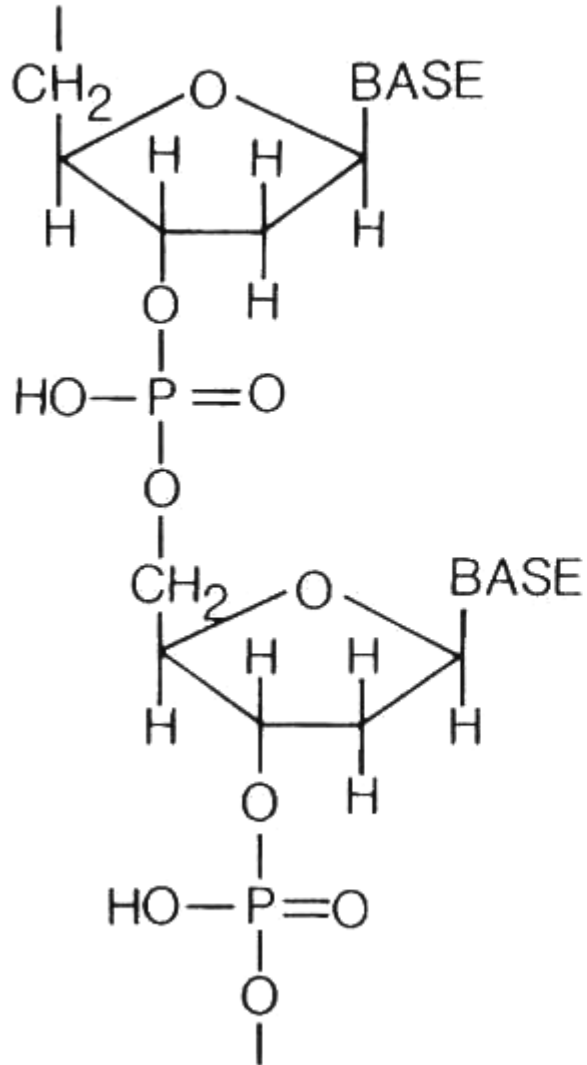
P Transformation

Chemical Fixation

P Cycling in Watershed

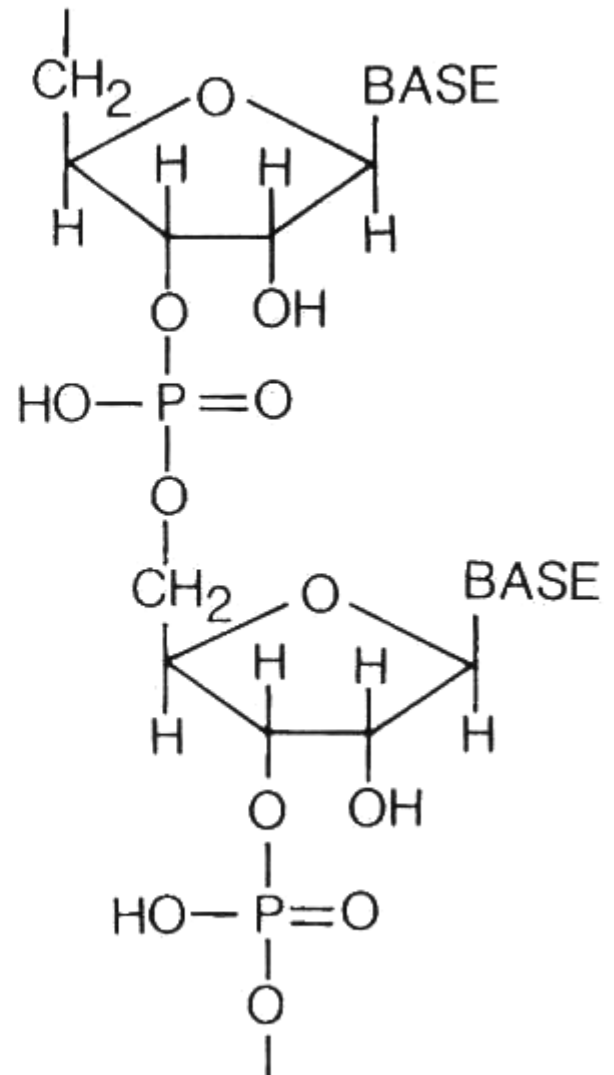
Summary

# DNA



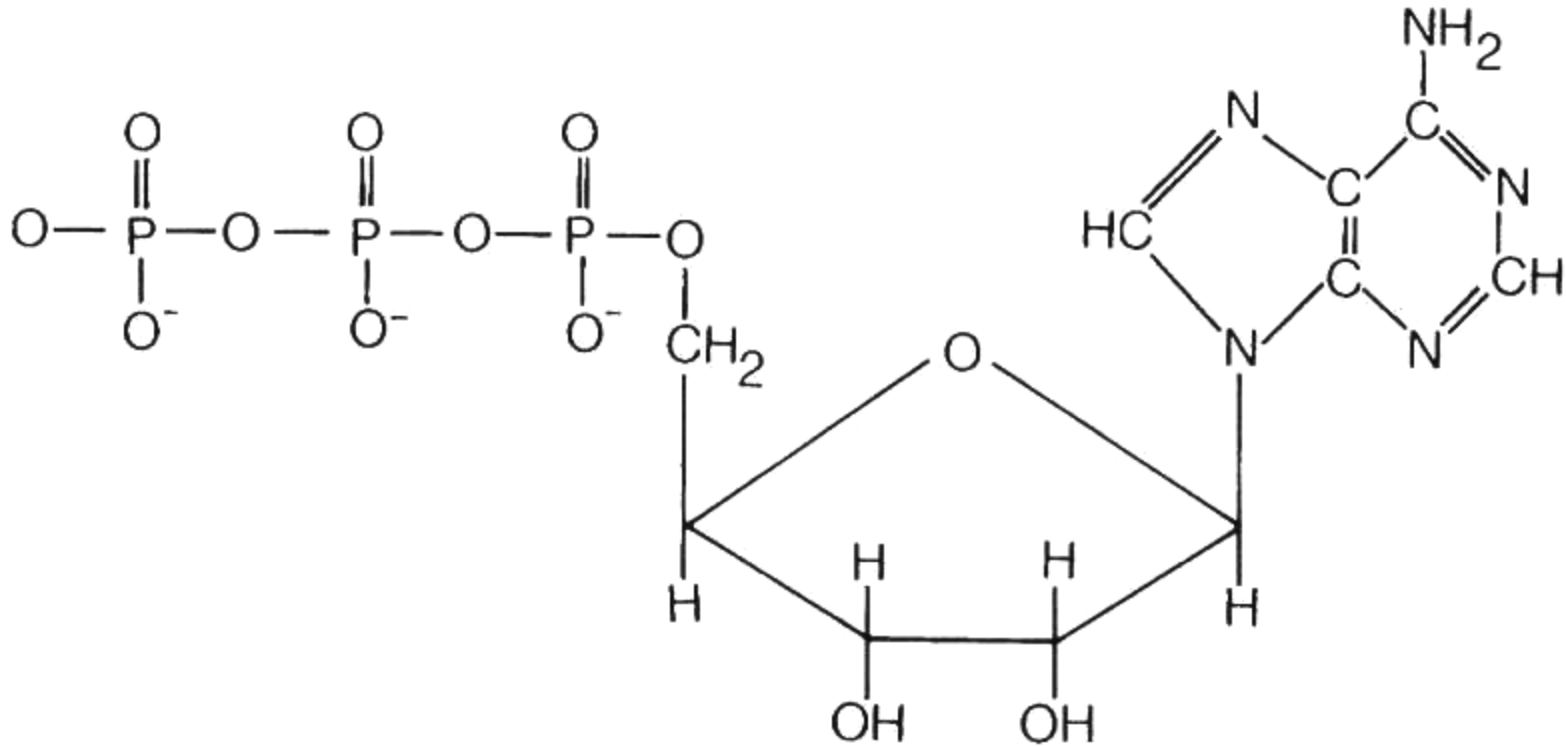
**deoxy-ribonucleic acid**

# RNA

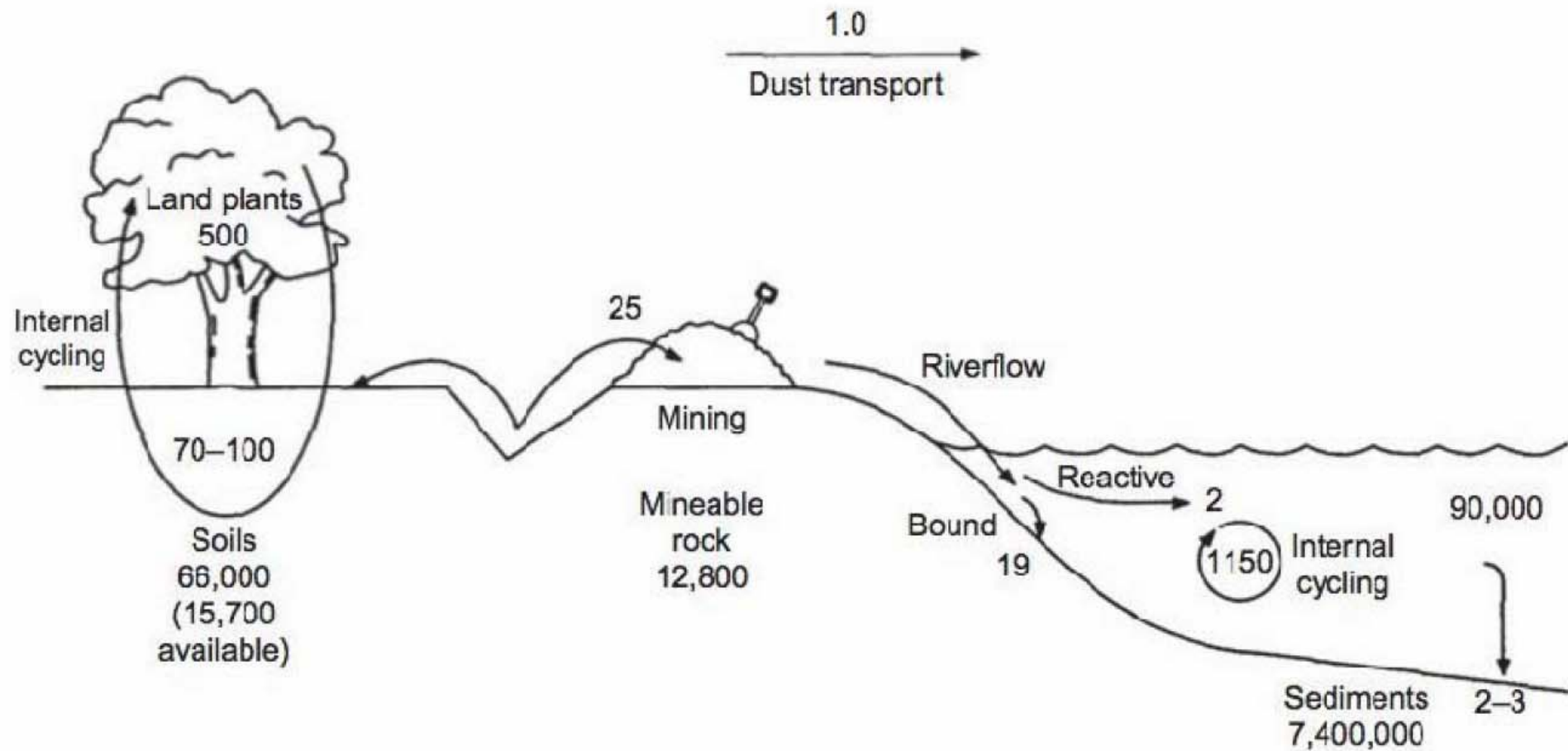


**ribonucleic acid**

# ATP (adenosine triphosphate)



On average, approximately 3% of dry living cells is made of phosphorus.



**FIGURE 12.7** The global phosphorus cycle. Each flux is shown in units of  $10^{12}$  g P/yr. Values for P production and reserves are taken from the U.S. Geological Survey. Estimate for sediments is from Van Cappellen et al. (1996), and estimates for other pools and flux are derived from the text.

## Table 14-2 The chemical formula of apatites

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General formula:  $\text{Ca}_{10}(\text{PO}_4)_6\text{X}_2$

$\text{X} = \text{F}^-$  Fluorapatite

$\text{OH}^-$  Hydroxyapatite

$\text{Cl}^-$  Chlorapatite

Possible substitutes for  $\text{Ca}^{2+}$ :

$\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  
 $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ , rare earth elements,  $\text{Bi}^{3+}$ ,  $\text{U}^{4+}$

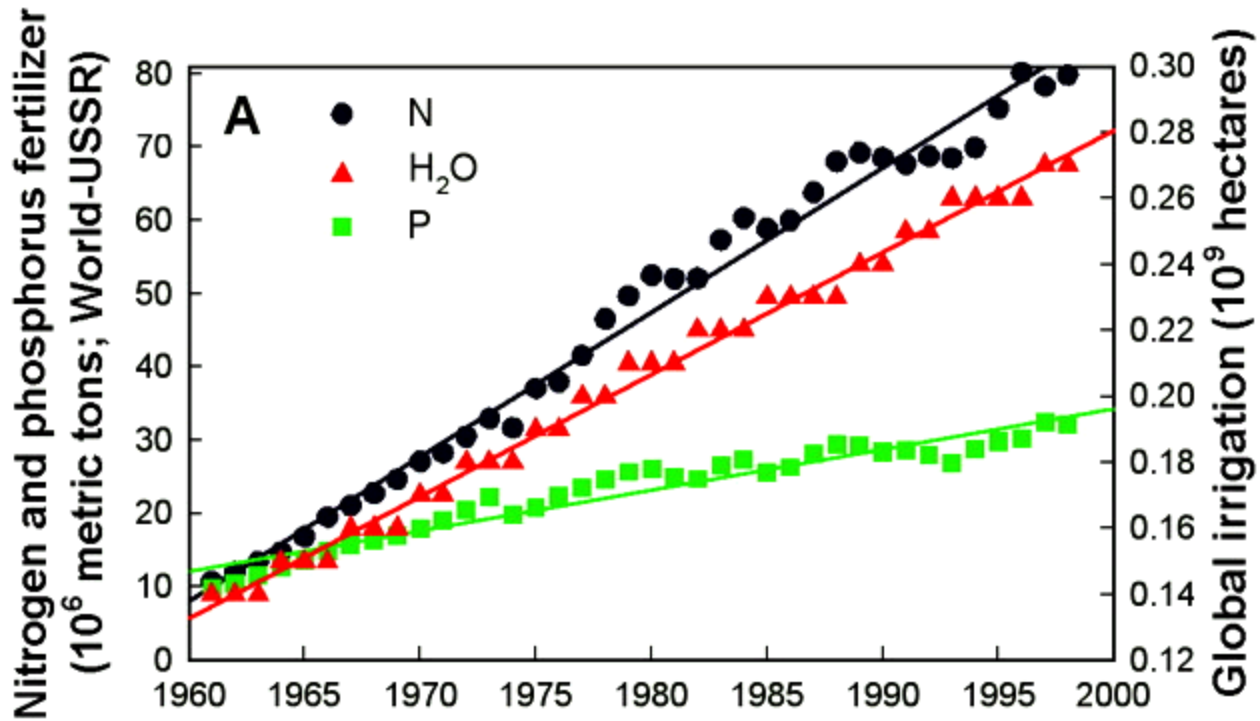
Possible substitutes for  $\text{PO}_4^{3-}$ :

$\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CrO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{VO}_4^{3-}$ ,  $\text{F}\cdot\text{CO}_3^{3-}$ ,  
 $\text{OH}\cdot\text{CO}_3^{3-}$ ,  $\text{SiO}_4^{4-}$

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From: Jacobson, Charlson, Rodhe & Orians, 2000

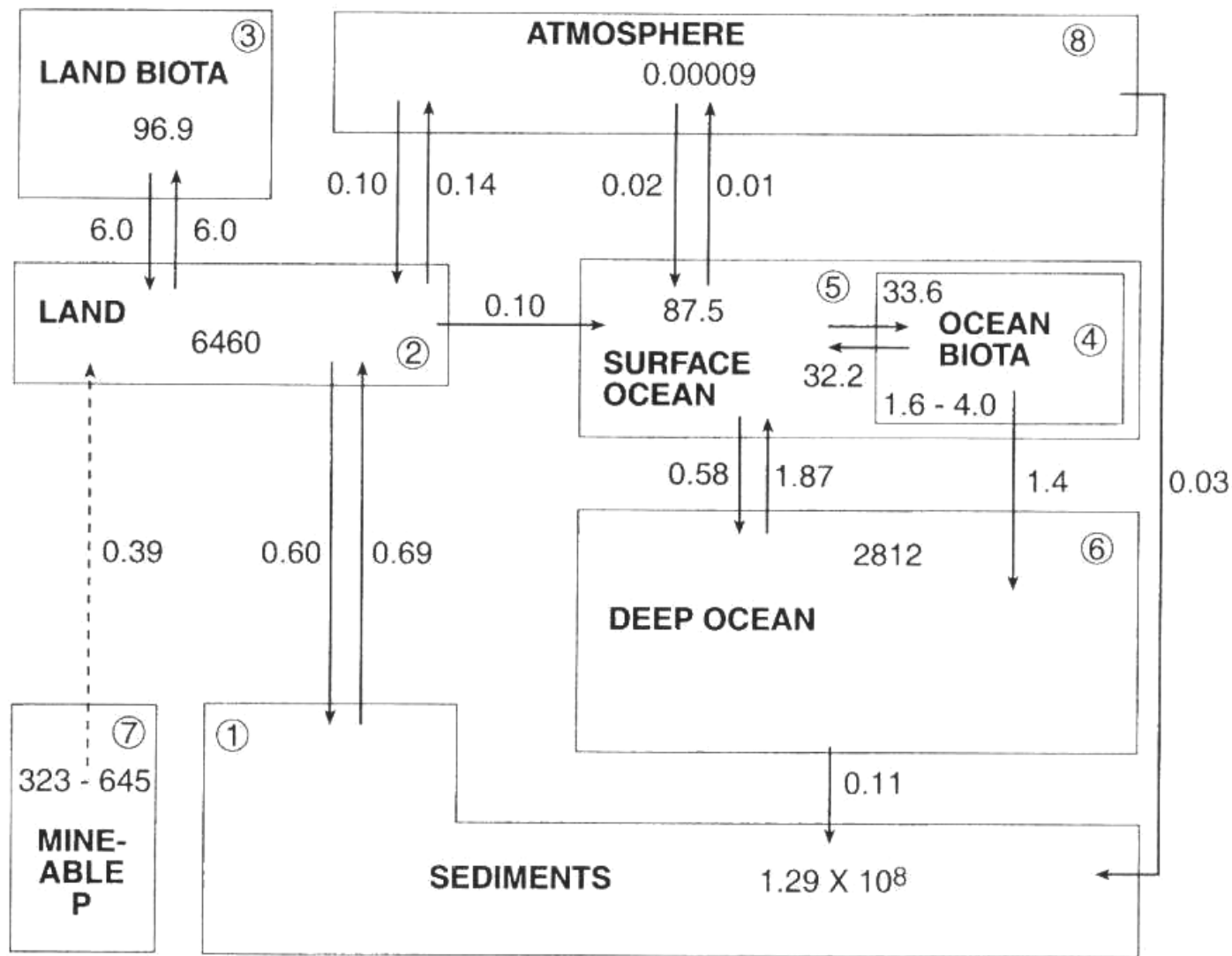
From: Tilman et al. 2001. Science 292:281-284



**Table 14-3** The mass of P in the major reservoirs (mol P  $\times 10^{-12}$ )

Reservoir	P content	Comments
1. Sediments	$1.29 \times 10^8$	Van Wazer (1961)
2. Land	6460	Computed from land area of $133 \times 10^6$ km <sup>2</sup> , soil thickness of 60 cm, density of 2.5 g/cm <sup>3</sup> and mean P content of 0.1% (Taylor, 1964)
3. Land biota	96.9	Computed from an estimate of the N in land biota ( $12 \times 10^4$ tons N; Delwiche, 1970); and a mean P:N atomic ratio in land plants (1.8:16; Deevey, 1970)
4. Oceanic biota	1.6–4.0	Mackenzie <i>et al.</i> (1993)
5. Surface Ocean	87.5	Computed from assumed mean concentration of 25 mg/m <sup>3</sup> of dissolved P, 300 m thick surface layer and area of $3.61 \times 10^8$ km <sup>2</sup>
6. Deep ocean	2812	Computed from assumed mean concentration of 80 mg/m <sup>3</sup> of dissolved P, a deep water thickness of 3000 m, and same surface area as above.
7. Mineable P	323–645	Mean values reported by Stumm (1973), Ronov and Korzina (1960) and Van Wazer (1961) and the value reported by Mackenzie <i>et al.</i> (1993)
8. Atmospheric	0.00009	Graham (1977)

From: Jacobson, Charlson, Rodhe & Orians, 2000



**Fig. 14-7** The global phosphorus cycle. Values shown are Tmol and Tmol/yr for reservoirs and fluxes, respectively. ( $T = 10^{12}$ ).



**Table 14-4** Summary of the flux of P between reservoirs (mol P  $\times 10^{12}$ )

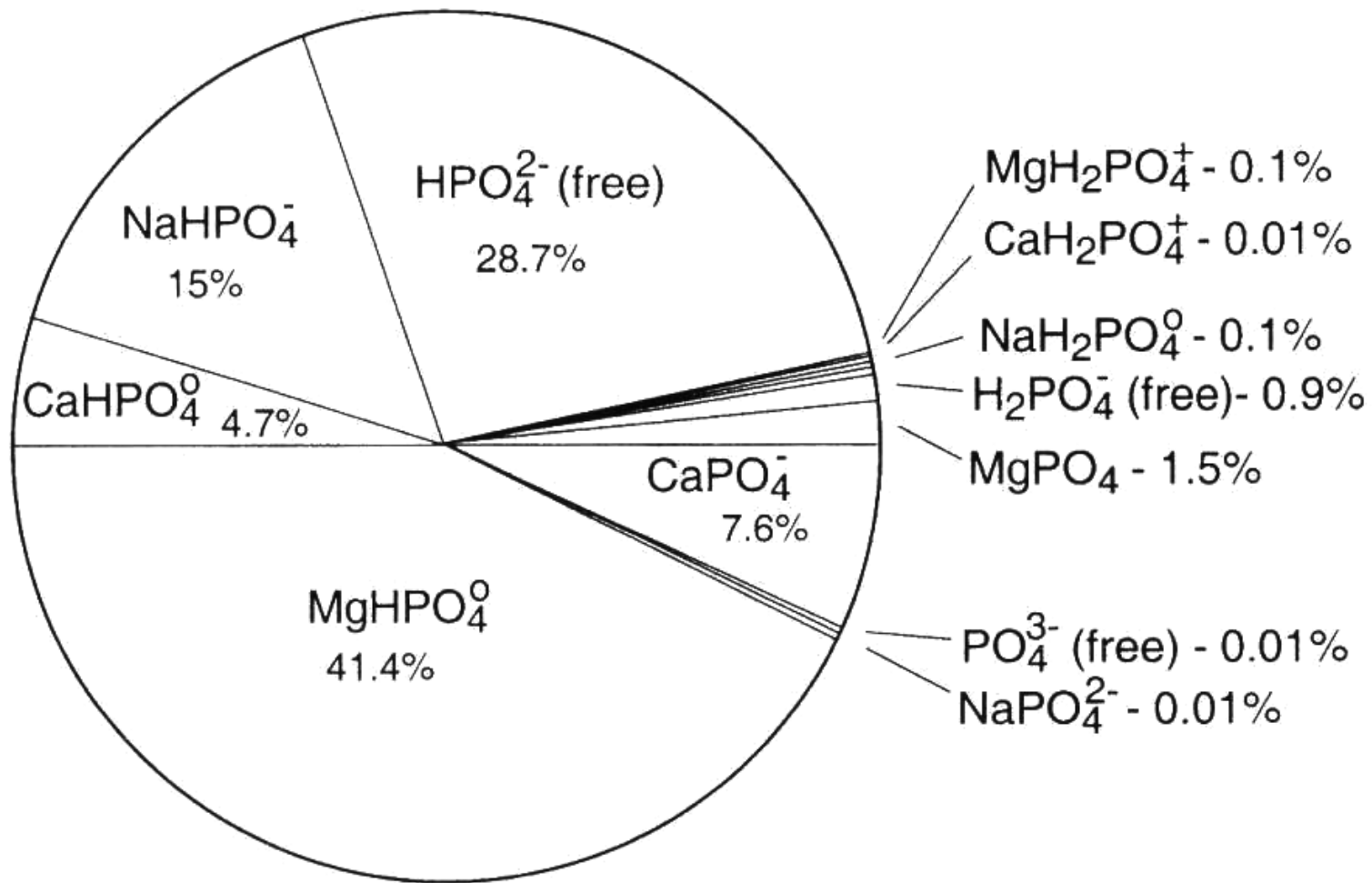
Transfer	Flux	Comments
$F_{12}$	0.69	Computed from combined rates of mechanical and chemical denudation of continents ( $2 \times 10^9$ tons/yr; Garrels and Mackenzie, 1971) and a mean P content of crustal material of 0.1% (Taylor, 1964)
$F_{23}, F_{32}$	6.00	Computed from total C fixed annually (560 Pg C/yr; Sundquist, 1993) and a mean P:C atomic ratio of land biota of 1:510 (Delwiche and Likens, 1977)
$F_{25}$	0.10	Garrels <i>et al.</i> (1973) and adjusting upward 33% to account for release from particles (after Kaul and Froelich, 1984)
$F_{54}$	33.6	Computed from rate of N fixation of oceanic biota of $7.5 \times 10^9$ tons N/yr (Vaccaro, 1965) and a mean P:N atomic ratio in ocean biota of 1:16 (Redfield <i>et al.</i> , 1963)
$F_{45}$	32.2	Computed assuming that 96% of oceanic biota recycled within upper 300 m
$F_{46}$	1.40	Difference between fluxes $F_{54}$ and $F_{45}$
$F_{56}$	0.58	Computed from the P content of surface layer given in Table 14-3 and a water exchange rate between surface and deep ocean of 2 m/yr (Broecker, 1971)
$F_{65}$	1.87	Computed as $F_{56}$ using the P content of the deep ocean given in Table 14-3
$F_{61}$	0.11	Calculated that the ocean is in steady state
$F_{72}$	0.39	Stumm (1973); Mackenzie <i>et al.</i> (1993)
$I'_{21}$	0.60	Mackenzie <i>et al.</i> (1993)
$F_{28}$	0.14	Graham (1977)
$F_{82}$	0.10	Graham (1977)
$F_{58}$	0.01	Graham (1977)
$F_{85}$	0.02	Graham (1977)
$F_{81}$	0.03	Graham (1977)

From: Jacobson, Charlson, Rodhe & Orians, 2000

**Table 14-5** Summary of reservoir amounts, total fluxes, and residence time

Reservoir	A (mol $\times 10^{-12}$ )	$\Sigma$ fluxes (mol a $^{-1}$ $\times 10^{-12}$ )	Residence time (years)
Atmosphere	0.00009	0.15	0.0006 (5.3 h)
Land biota	96.9	6.0	16.2
Land	6460	9.81	949
Surface ocean	87.5	34.2	2.56
Ocean biota	1.6–4.0	33.6	0.048–0.19 (18–69 d)
Deep ocean	2812	1.98	1420
Sediments	$1.29 \times 10^8$	0.71	$1.82 \times 10^8$
Total ocean system	2902	0.12	24 180

From: Jacobson, Charlson, Rodhe & Orians, 2000



**Fig. 14-2** Calculated speciation of  $\text{PO}_4^{3-}$  in seawater of 34.8 parts per thousand salinity at  $20^\circ\text{C}$  and a pH of 8.0 (Atlas, 1975).

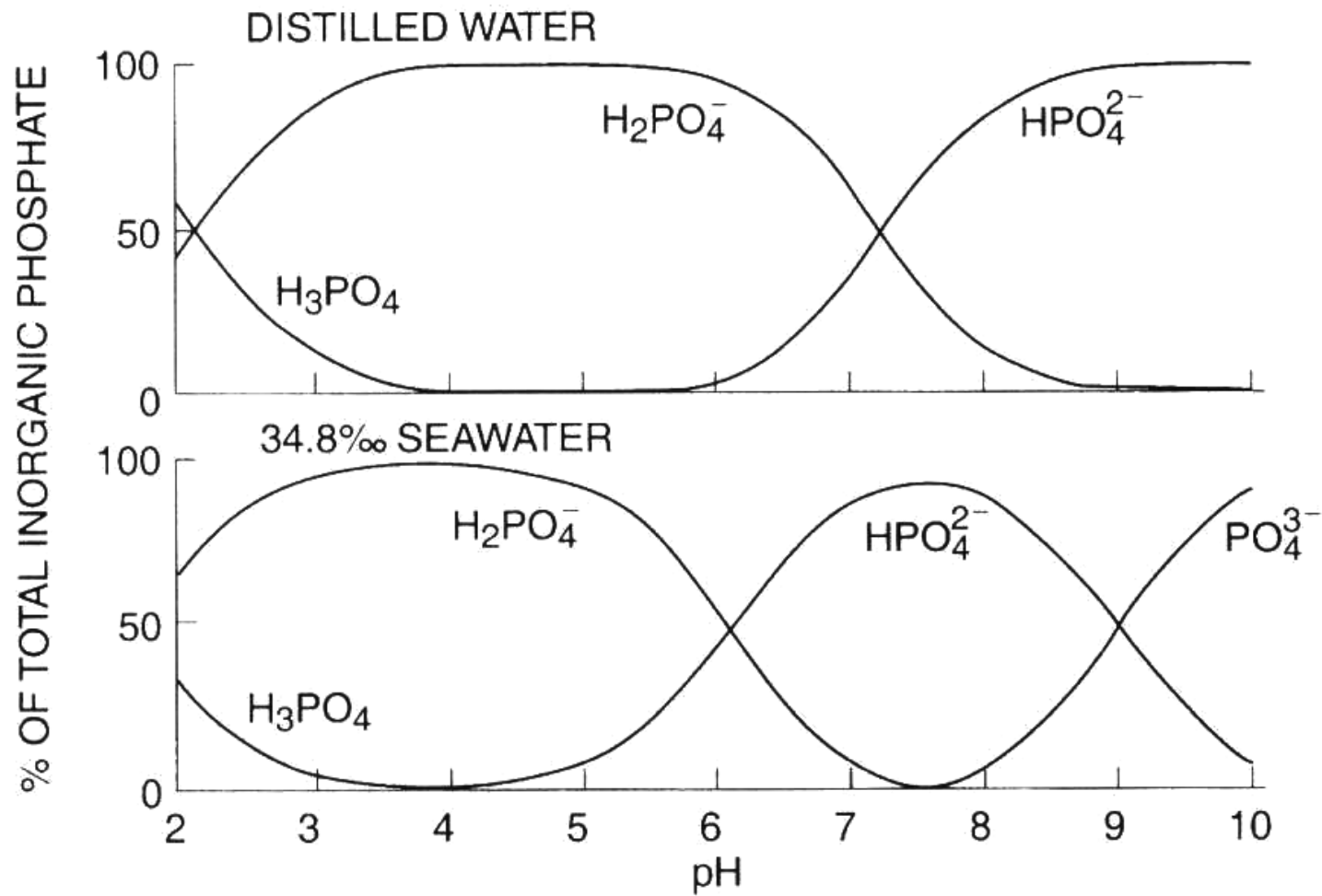
From: Jacobson, Charlson, Rodhe & Orians, 2000

**Table 14-1** Dissociation constants of phosphoric acid at 25°C

	Distilled water <sup>a</sup> (pK)	Seawater <sup>b</sup> (pK)
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$	2.2	1.6
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$	7.2	6.1
$\text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$	12.3	8.6

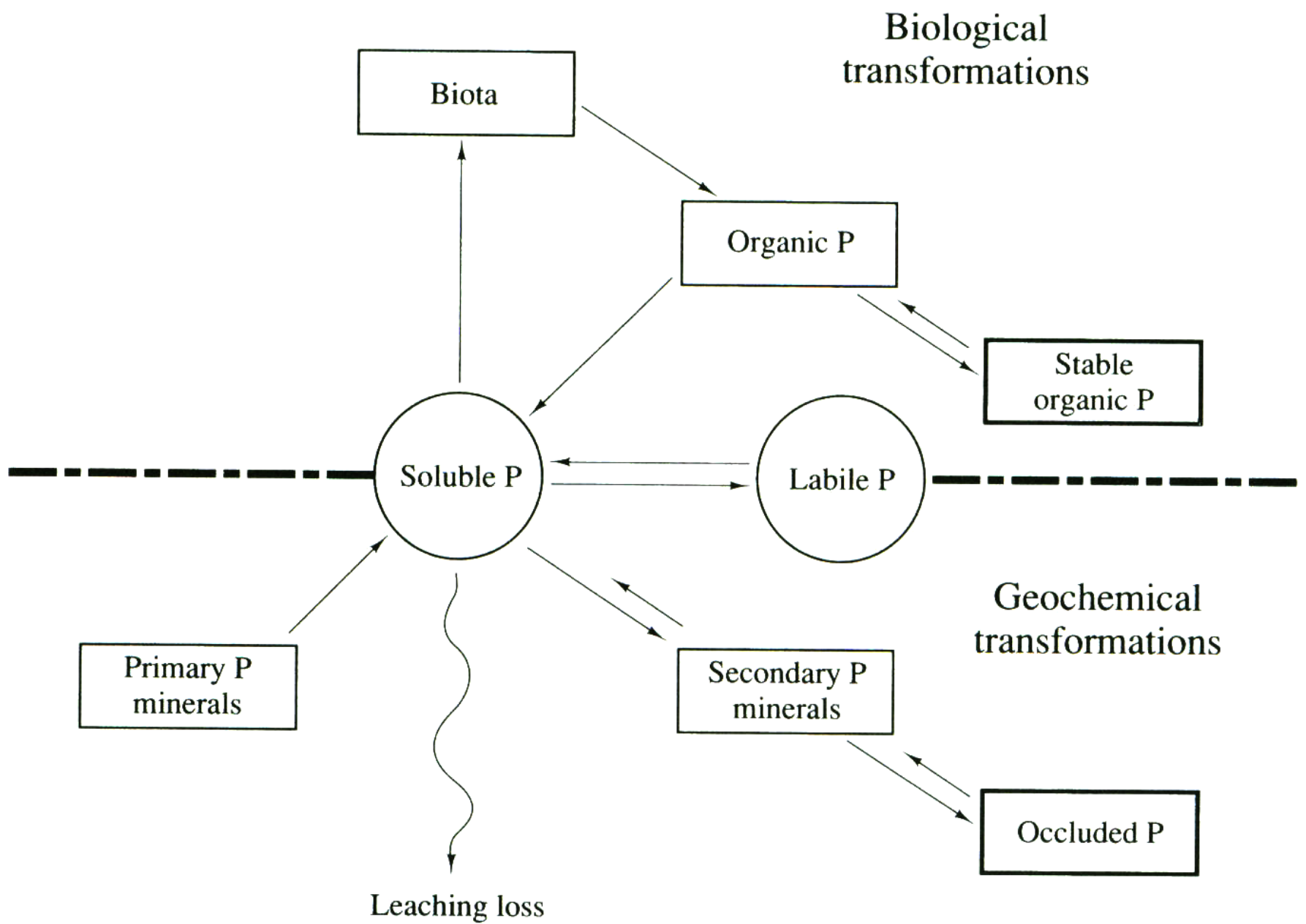
<sup>a</sup> Stumm and Morgan (1981).

<sup>b</sup> Atlas (1975).



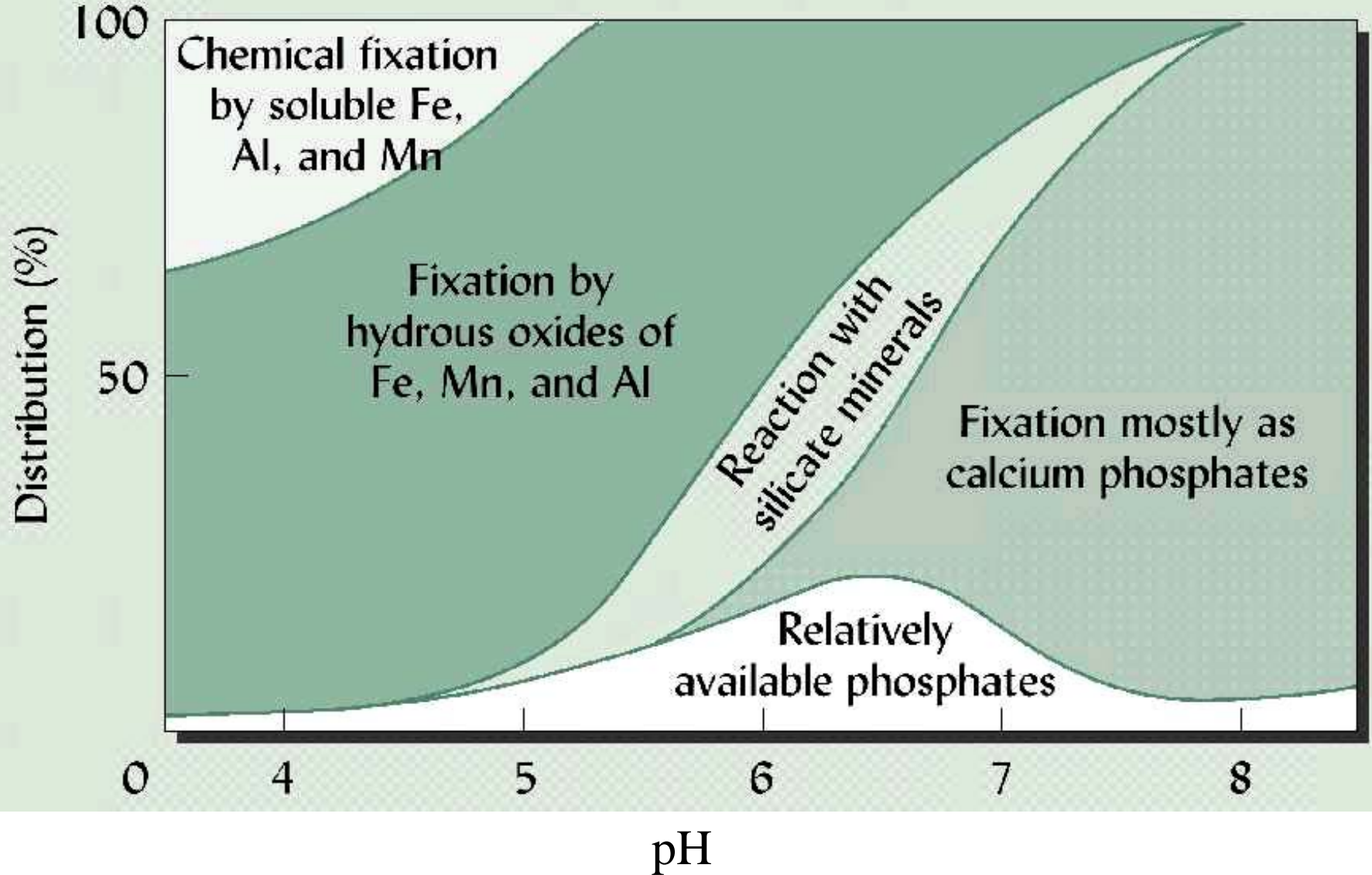
**Fig. 14-1** Extent of dissolution of phosphoric acid species as a function of pH in distilled and sea waters (Atlas, 1975).

From: Jacobson, Charlson, Rodhe & Orians, 2000



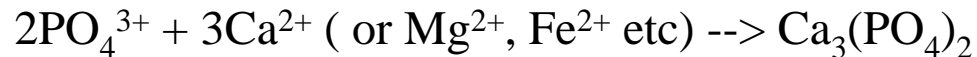
**Figure 6.17** Phosphorus transformations in the soil. From Smeck (1985).

# Chemical P fixation is pH-dependent.



# Fixation and Mobilization of Phosphorus

Phosphorus is easily fixed by chemical reactions with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$  etc. Phosphorus fixation is pH-dependent, and is the process that removes P from active pools. Both too high and too low of pH values can result in P fixation, for example:

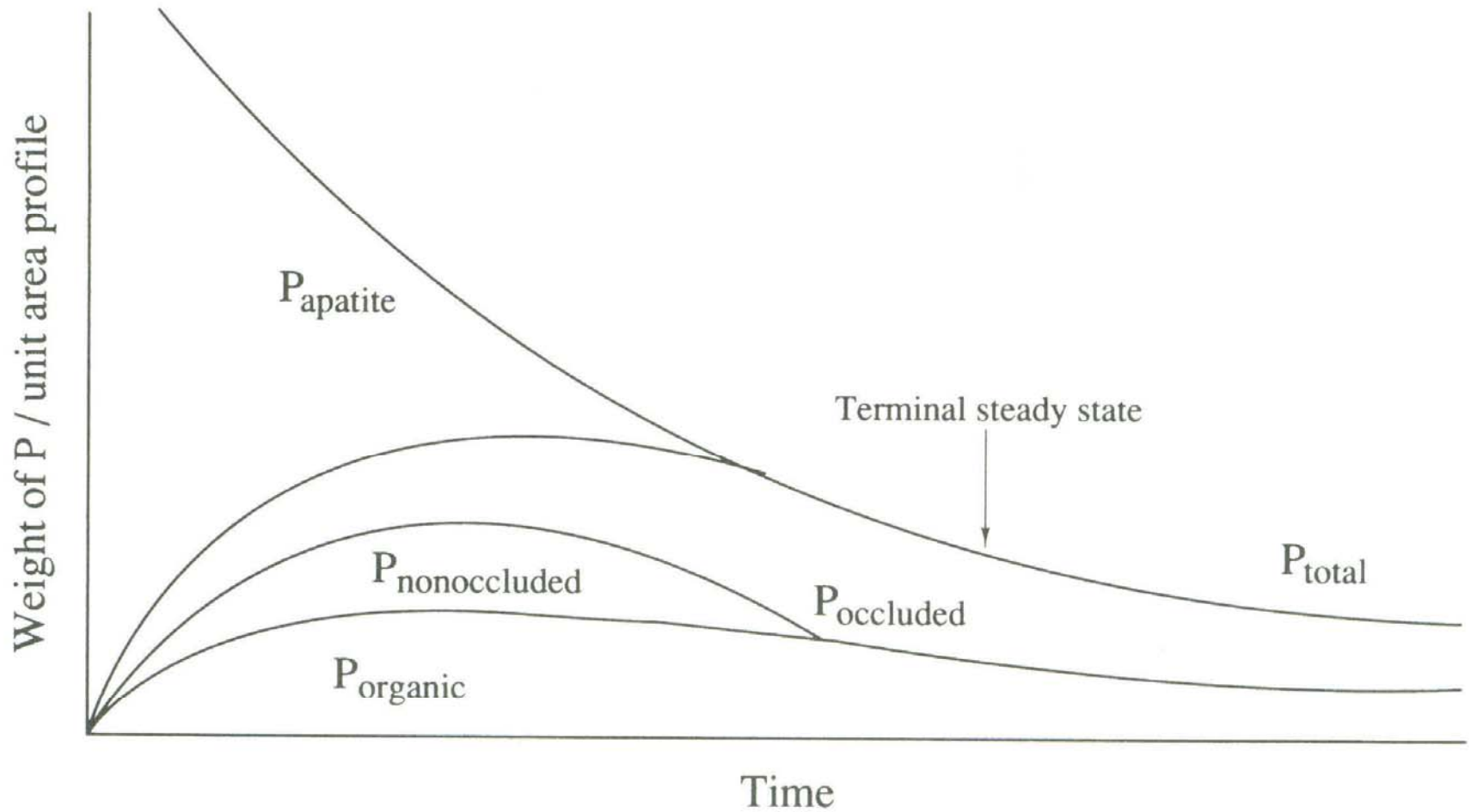


This is solely a chemical process.

Although the total P content of soils is large, in most soils only a small fraction is available to biota, primarily because of chemical fixation.

Microbes play a crucial role in the transforming process from organic P to inorganic P, and in mobilizing chemically-fixed P (mycorrhizal roots and other rhizosphere activities).





**Figure 4.5** Changes in the forms of phosphorus found during soil development on sand dunes in New Zealand. Modified from Walker and Syers (1976).

**TABLE 13.** Summary of Annual Input–Output Budgets for Forested Ecosystems at Hubbard Brook.<sup>a</sup>

Element	Input, kg/ ha·yr	Output, kg/ha·yr	Net gain (+) or loss (–), kg/ha·yr
Si	—	23.8	–23.8
Ca	2.2	13.9	–11.7
Na	1.6	7.5	–5.9
Al	—	3.4	–3.4
Mg	0.6	3.3	–2.7
K	0.9	2.4	–1.5
Organic C	1484 <sup>b</sup>	12.3	+1472
N	20.7	4.0	+16.7
Cl	6.2	4.6	+1.6
S	18.8	17.6	+1.2
H	0.96 <sup>c</sup>	0.10 <sup>c</sup>	+0.86
P	0.036	0.019	+0.017

<sup>a</sup>Input values for organic C, N, and S include bulk precipitation and estimates of dry deposition; all others are based on bulk precipitation only. Output values include both dissolved substances (Table 10) and particulate matter (Table 9) in stream water.

<sup>b</sup>Includes ecosystem biomass accretion (*net ecosystem gaseous uptake of CO<sub>2</sub>*) based on the period 1961–1965 (Whittaker et al., 1974); therefore output does not include respiration losses of CO<sub>2</sub>.

<sup>c</sup>Dissolved form only.

**TABLE 21.** Standing Stocks and Annual Biogeochemical Fluxes for a 55-yr old Forested Ecosystem at Hubbard Brook.

Component	Chemical Element							
	Ca	Mg	Na	K	N	S	P	Cl
	Standing stock (kg/ha)							
Aboveground biomass	383	36	1.6	155	351	42	34	*
Belowground biomass	101	13	3.8	63	181	17	53	*
Forest floor	372	38	3.6	66	1256	124	78	*
	Annual flux (kg/ha·yr)							
Bulk precipitation input	2.2	0.6	1.6	0.9	6.5	12.7	0.04	6.2
Gaseous or aerosol input	*	*	*	*	14.2	6.1	*	?
Weathering release	21.1	3.5	5.8	7.1	0	0.8	?	*
Streamwater output								
Dissolved substances	13.7	3.1	7.2	1.9	3.9	17.6	0.01	4.6
Particulate matter	0.2	0.2	0.2	0.5	0.1	<0.1	0.01	*
Vegetation uptake	62.2	9.3	34.8	64.3	79.6 <sup>a</sup>	24.5 <sup>a</sup>	8.9	*
Litter fall	40.7	5.9	0.1	18.3	54.2	5.8	4.0	*
Root litter	3.2	0.5	0.01	2.1	6.2	0.6	1.7	*
Throughfall and stemflow	6.7	2.0	0.3	30.1	9.3	21.0	0.7	4.4
Root exudates	3.5	0.2	34.2	8.0	0.9	1.9	0.2	1.8
Net mineralization	42.4	6.1	0.1	20.1	69.6	5.7	?	?
Aboveground biomass accretion	5.4	0.4	0.03	4.3	4.8	0.8	0.9	*
Belowground biomass accretion	2.7	0.3	0.12	1.5	4.2	0.4	1.4	*
Forest floor accretion	1.4	0.2	0.02	0.3	7.7	0.8	0.5	*

\*small, unmeasured

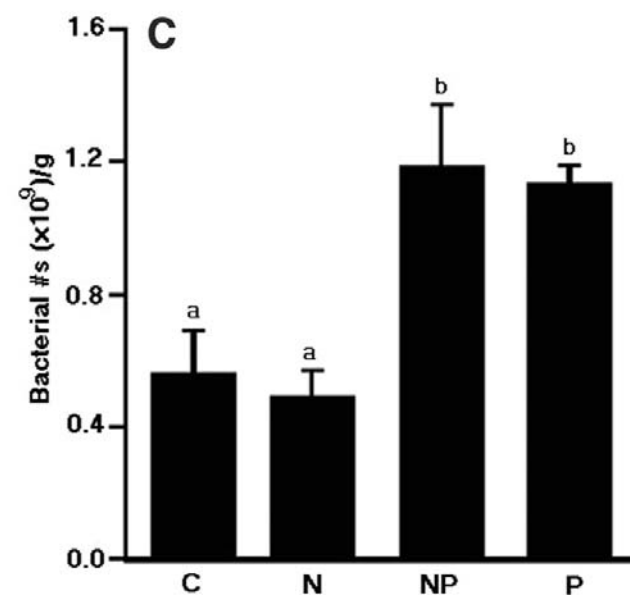
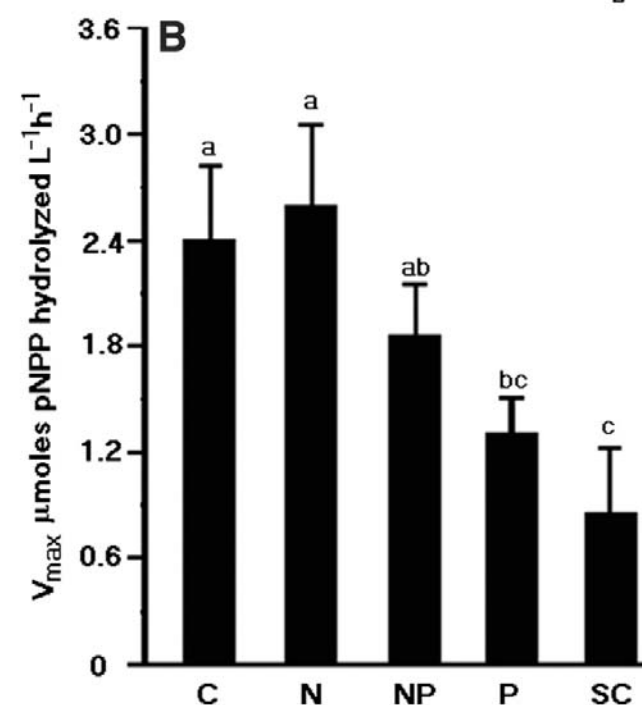
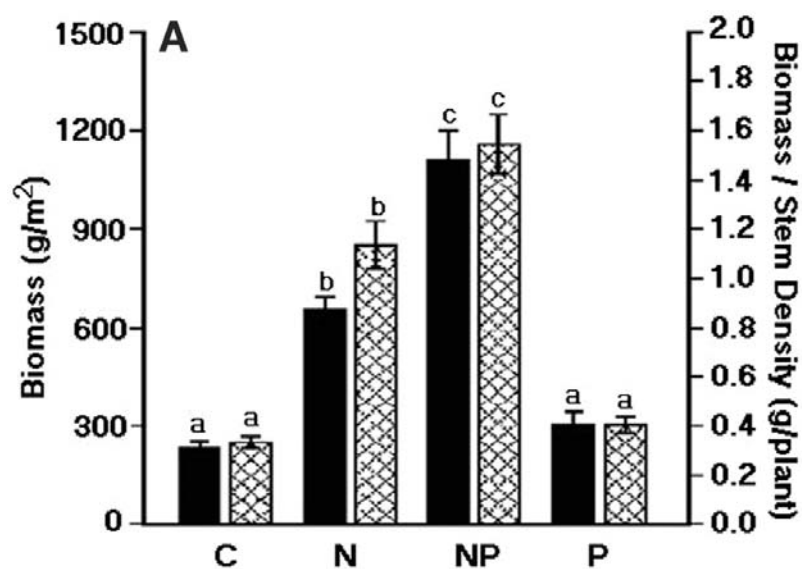
<sup>a</sup>root uptake

## P-enrichment of the Everglades

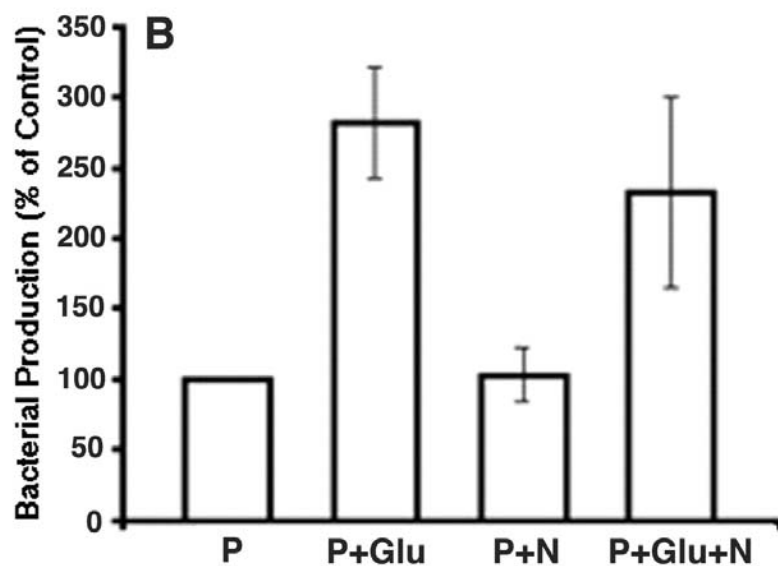
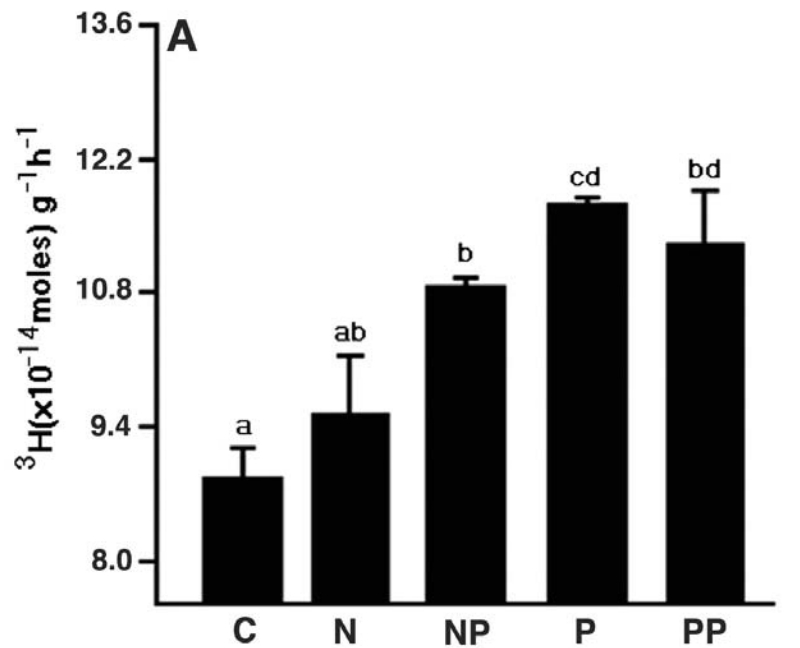




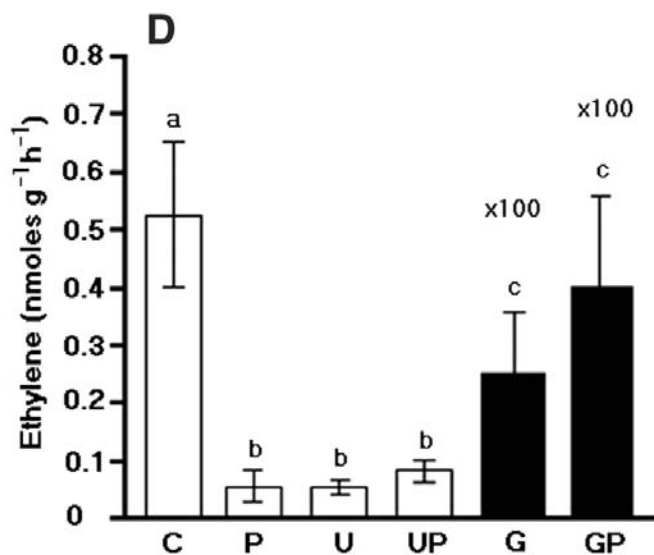
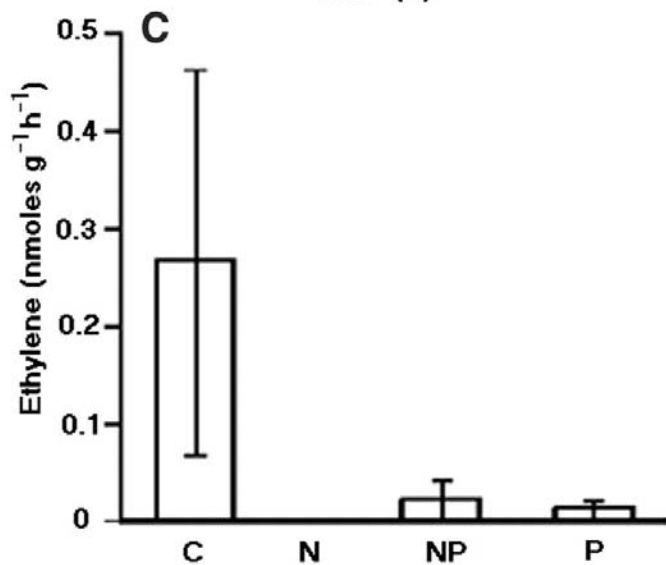
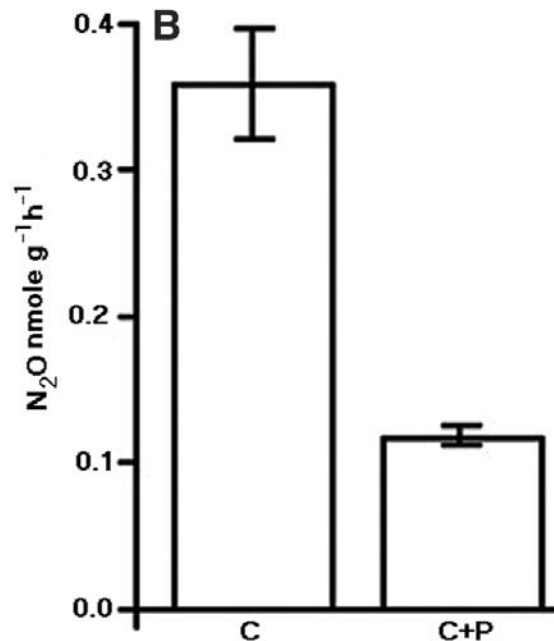
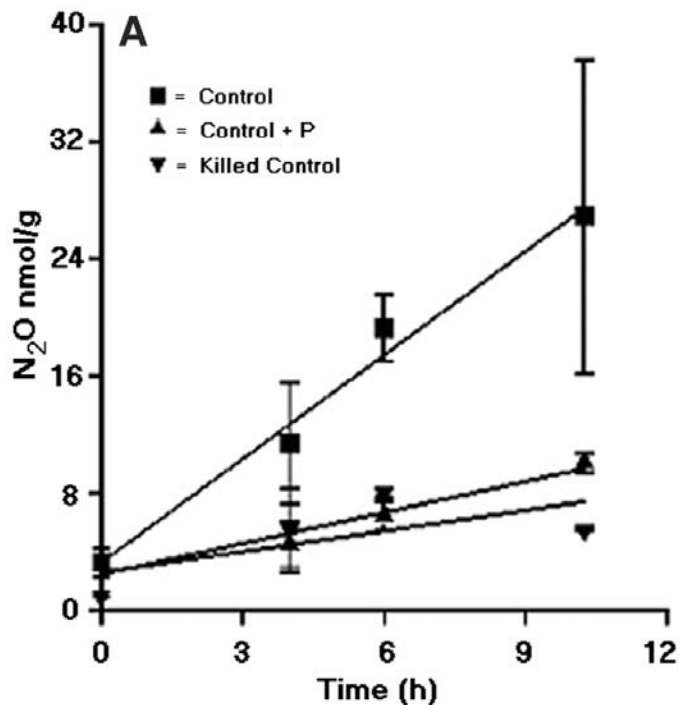
Florida's Everglades is a region of broad, slow-moving sheets of water flowing southward over low-lying areas from Lake Okeechobee to the Gulf of Mexico. In places this remarkable 'river of grass' is 80 kilometers wide. These images from the Multi-angle Imaging SpectroRadiometer show the Everglades region on January 16, 2002. Each image covers an area measuring 191 kilometers x 205 kilometers.



**Figure 1.** Response of ecosystem processes to treatments. Treatment N was nitrogen applied at 30 mol m<sup>2</sup> year<sup>-1</sup> as ammonium nitrate fertilizer; treatment NP, nitrogen plus phosphorus applied at 30 mol m<sup>2</sup> year<sup>-1</sup> as ammonium nitrate and 15 mol m<sup>2</sup> year<sup>-1</sup> as phosphate fertilizer, respectively; treatment P, phosphorus applied at 15 mol m<sup>2</sup> year<sup>-1</sup> (as phosphate fertilizer); and treatment C, control. Means that are not significantly different ( $\alpha = 0.05$ ) are labeled with the same lower-case letter. **(A)** Mean [ $\pm 1$  SE,  $n = 6$  (where  $n$  indicates the number of 0.25 m  $\times$  0.25 m quadrants)] end-of-season above-ground standing biomass (solid) and biomass per ramet (hatched) of *Spartina alterniflora* as a function of nutrient treatment. **(B)** Mean ( $\pm 1$  SE) maximum velocity ( $V_{\max}$ ) of pore-water phosphatase enzyme activity in the rooting zone (0 to 25 cm) from fertilized plots in a North Inlet marsh and from a contrasting salt marsh (SC) located at the mouth of the urbanized Cooper River estuary in South Carolina. Enzyme activity was assayed spectrophotometrically (with the use of p-nitrophenylphosphate as substrate) (11) in triplicate at in situ pH monthly for 10 months. **(C)** Effect of nutrient treatments on mean ( $\pm 1$  SE,  $n = 3$ ) bacterial abundance in surface sediment (0 to 5 cm).



**Figure 2.** (A) Effects of nutrient treatments on rates (mean  $\pm$  1 SE,  $n = 6$ ) of thymidine incorporation into bacteria in North Inlet salt marsh sediment. Treatments N, NP, and P were nitrogen, nitrogen plus phosphorus, and phosphorus, respectively, whereas treatment PP was a phosphorus amendment in the form of pyrophosphate. (B) Rates (mean  $\pm$  1 SE,  $n = 6$ ) of thymidine incorporation into bacteria in sediments fertilized in the field with phosphorus. Treatment P was a control (unaltered in the lab); treatment P+Glu, an addition of glucose in the lab; treatment P+N, an addition of nitrogen; and treatment P+Glu+N, an addition of glucose and nitrogen.



**Figure 3.** (A) Rates (mean  $\pm$  1 SD,  $n = 2$ ) of potential denitrification (acetylene block) per weight of dry sediment in laboratory incubations of sediment from field controls amended with nitrate (5 mM final concentration) either with or without added phosphorus (200  $\mu$ M). (B) Rates (mean  $\pm$  1 SD,  $n = 2$ ) of potential N<sub>2</sub>O production (without acetylene) per weight of dry sediment in laboratory incubations of sediment amended with nitrate (20 mM final concentration) either with or without added phosphorus (400  $\mu$ M). (C) Rates (mean  $\pm$  1 SE,  $n = 6$ ) of nitrogen fixation in field controls (C) and in field treatments as in Fig. 1. (D) Rates (mean  $\pm$  1 SE,  $n = 3$ ) of nitrogen fixation in sediments from field controls amended in the lab with glucose (G), urea (U), or phosphorus (P). All additions were made to 10 mM final concentration. Nitrogen fixation rates were greater in the presence of glucose (solid bars) than without. Multiply the scale by 100 for bars labeled "x100." Significance of treatment effects, determined on log-transformed data, is denoted by different letters



# Summary of the Phosphorus Cycle

- 1.** There is no significant gaseous component, transfer in the air is in particulates or sea spray.
- 2.** There is no change in valence, all in phosphate form.
- 3.** It is believed that all original P came from rock weathering.
- 4.** Microbes play a role in the process from organic P to inorganic P, and in mobilizing chemically fixed P (mycorrhizae and rhizosphere activities)
- 5.** P is easily fixed by chemical reactions with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$  etc. The process that removes P from active pools. Both too high and too low of pH values can result in P fixation.
- 6.** Although the total P content of soils is large, in most soils only a small fraction is available to biota, primarily because of chemical fixation.
- 7.** Mining the P from apatite ( $3\text{Ca}_3[\text{PO}_4]_2 \cdot \text{Ca}[\text{FeCl}]_2$ ) is the main source of P fertilizer (about 14 million metric tons per year).
- 8.** Through geologic time (hundreds of millions of years), P-containing sediments are buried, uplifted and subject to rock weathering, completing the global cycle.