

Lacustrine sediment/groundwater nutrient dynamics

J.M. COLEMAN¹ and E.S. DEEVEY²

¹Environmental Management, Inc., 5003 Riveredge Drive, Titusville, FL 32780, USA

²Florida State Museum, University of Florida, Gainesville, FL 32611, USA

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Abstract. A small pond in southwestern peninsular Florida was sampled to determine the areal and depth distribution of total phosphorus, total nitrogen, and organic matter. Concentrations of these constituents decreased from the center to the edge of the pond and from the top to the bottom of the sediments. At the center of the pond total phosphorus showed a secondary concentration peak at a depth of 20 to 40 cm in the sediments indicative of the downward transfer of soluble phosphorus during times of low water.

A system of monitoring wells was installed at the pond to measure groundwater input and output nutrient concentrations. There was no difference in total groundwater nitrogen concentration across the pond but the mean increase in total phosphorus concentration between input and output wells, ca. $200 \mu\text{g l}^{-1}$, was statistically highly significant. The results suggest that whereas nitrogen is recycled from sediments to the pond and the atmosphere, the pond-sediment system loses some phosphorus to groundwater throughflow.

Introduction

At and just below the sediment-water interface where some lacustrine organic matter is mineralized and some nutrients are released, organic decomposition and nutrient exchange have been extensively studied by geologists (e.g., Barnes and Barnes, 1978) and limnologists (see symposium volumes edited by Golterman, 1977, and Sly, 1982, and review by Binford, et al., 1983). Below the active layer, however, although lake sediments are well known to be a sink for organic carbon and nutrients, and particularly for phosphorus (Deevey, 1984; Deevey, et al., 1980), the permanence of storage has rarely been considered. Some evidence that diagenesis continues in sediments as old as several millenia appears in organic sections overlying coarse sand (Lindeman, 1941; Deevey and Brenner, 1976), but the fate of the lost materials was not followed in these studies. We have conducted an experimental study to learn whether the sediment sink is completely tight or whether some mobile fraction of sedimented nutrients is exchanged with moving ground water.

One of the striking features of the pine flatwoods in many parts of Florida is the number of subcircular depressions or ponds that dot the landscape. In Sarasota County, excluding the coastal strand, the average

density of ponds is 6 to 8 per square kilometer. They range in size from a fraction of a hectare to many hectares. The ponds are shallow, one-half to a few meters deep, and contain water for much of the year. During the dry season (spring) only the deeper ponds retain water but in the wet season (late summer) water may rise above the rims of the ponds and extend many meters into the pine flatwoods proper. Because of their small size and relatively simple hydrology these ponds are promising subjects for studies of sediment/groundwater nutrient interactions.

This study was designed to answer two specific questions. Does phosphorus leave lacustrine systems by way of ground water, and if so, at what rate? Secondly, with regards to nitrogen, is the relationship between lacustrine sediments and the atmosphere a closed cycle, or is there a flow-through component via the ground water? The approach used to answer these questions was to determine the distribution of total phosphorus and total nitrogen in the sediments and compare these to concentrations in the ground water.

Description of the study pond

The pond used for this study was chosen on the basis of its remoteness and natural setting, in a lightly forested region showing no signs of recent fires or significant human influences. It is located in southern Sarasota County, Florida between the Peace and Myakka Rivers, in the mid-peninsular Gulf of Mexico coastal lowlands (White, 1970). This region is extremely flat with a very gentle slope in a generally southwesterly direction. In the immediate vicinity the slope is to the south-southwest at an approximate rate of one meter per thousand.

The pond occupies a depression in the medium to fine-grained surficial sands (approximately 3 m thick) which unconformably overlie the one-meter thick Caloosahatchee Formation, a sandy shell marl (Brooks, 1968). The pond is nearly circular, has a radius of slightly more than 50 m, and a depth at the center of about 80 cm. As viewed in cross-section the sediment lens is hypersinusoidal in shape, with a maximum thickness at the center of 83 cm, tapering to a few cm at the edges. The sediment/sand boundary is very well defined by differences in organic matter content, color, and grain-size distribution. There are no inflowing nor outflowing streams and no perceptible artesian influences. Seasonal fluctuations in water level are apparently due solely to the effects of precipitation and evaporation on the water table. Net accumulation of sediment in the pond began about 5,000 ^{14}C years ago (4565 ± 120 , University of Miami Radiocarbon Dating Laboratory #UM-1494), most likely as a result of a rise of the groundwater table, in turn mediated by sea-level rise (Scholl, et al., 1969).

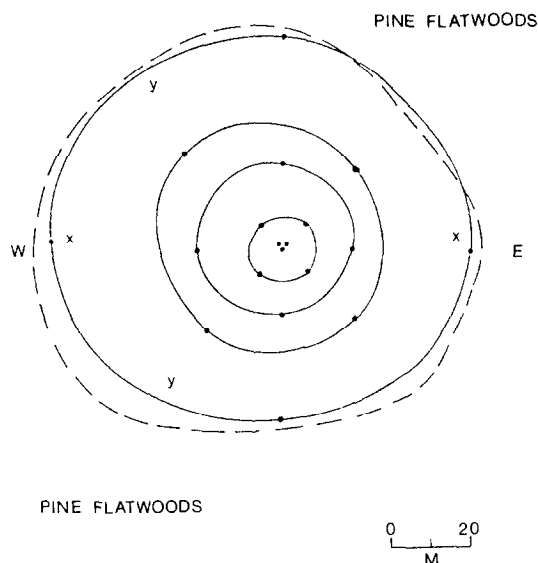


Figure 1. Areal view of study pond showing location of sediment cores (•) and groundwater sampling wells. x = location of battery of four replicate wells. Wells are on transects perpendicular to the east-west line through the center of the pond, and are spaced 2 m apart. y = location of single outlier wells installed to ensure against the possibility of anomalous groundwater flow (see text). Solid lines = 20 cm contour intervals; broken line = pond/pine flatwoods boundary.

The pond supports an interesting array of aquatic and emergent macrophytic vegetation, arranged around the pond center in concentric and nearly monotypic communities. The yellow pondlily, *Nuphar luteum* (L.) Sibthorp and Smith, occupies the pond center. Concentrically arranged around the center is the spikerush community of *Eleocharis baldwinii* (Torrey) Chapman, in turn surrounded by maidencane, *Panicum hemitomon* Schultes. The outer ring is dominated by sandcypress (*Hypericum fasciculatum* Lamarck), dog fennel (*Eupatorium capillifolium* (Lamarck) Small), and beardgrass (*Andropogon glomeratus* (Walter) BSP). Vegetation is described in greater detail by Coleman (1979).

Distribution of nutrients in the sediments

Methods

The pond sediments were sampled with a coring device consisting of a polycarbonate tube, 4.5 cm i.d., ca. 3 m long, and containing a piston to ensure recovery of the complete core and preservation of stratigraphy. The sampling scheme consisted of three center cores and four cores each in four concentric rings, at intervals of 20 cm of elevation out from the center (Figure 1). As a result of the hypersinusoidal shape of the sediment lens,

as viewed in cross-section, core lengths ranged from 83 cm at the center to a few cm at the edges. The nineteen cores were cut into 5 cm segments which resulted in 172 samples. These were oven-dried at 105 °C for 20 hours (Black, et al., 1965). Longer drying times were tried with no additional water loss. The organic matter content of the sediment samples was determined by loss on ignition in a muffle furnace for one hour at 550 °C. Longer ignition times resulted in no additional weight loss.

Total phosphorus and total nitrogen concentrations were determined by the following methods. Sediment samples were digested by concentrated sulfuric acid and hydrogen peroxide in a heated block digester (modified from EPA, 1974). Fisher high-temperature bath oil was added to the digester prior to inserting the digestion tubes in order to ensure uniform heating of the samples. The samples were subsequently analyzed for total nitrogen and total phosphorus by the indophenol and ammonium molybdate/ascorbic acid methods, respectively (EPA, 1974). About 20% of the samples were run in triplicate and the resulting average deviation about the mean was 6% for organic matter and both nutrients. In addition to these standard laboratory procedures, method-quality assurance for phosphorus was maintained during the chemical analysis program by periodic analyses of the National Bureau of Standards Standard Reference Material, green cement. Average recovery of phosphorus from 24 samples of this material was 99.6% with standard deviation of 7% of the mean.

Results

Cores were grouped into rings of equal elevation (Figure 1) after it was determined that intra-ring statistical variation was small relative to inter-ring variation, thereby indicating that although organic matter, nitrogen, and phosphorus distributions, as expected, vary radially out from the center of the pond they do not vary substantially between radii. Figure 2 shows the mean distribution of organic matter, total nitrogen, and total phosphorus under 1 cm² surface area of sediments, with respect to depth and radial distance from the center of the pond. Organic matter content drops sharply in the top 10 cm in the center portion of the pond, represented by the first two graphs in Figure 2a, and then stabilizes at a concentration of about 80 mg cc⁻¹ until near the bottom of the sediments, where the concentration decreases again. Away from the center and out to the edge of the pond, OM content drops precipitously for about 20 cm and then stabilizes at 10 to 30 mg cc⁻¹, which is the organic matter content of the sandy flatwood soils surrounding the pond (see, for example, Immokalee soil, USDA Soil Conservation Service, 1977).

Total nitrogen distribution in the sediments (Figure 2b) follows fairly closely the pattern of organic matter content. This indicates that as organic matter decomposes bound nitrogen compounds are freed and become

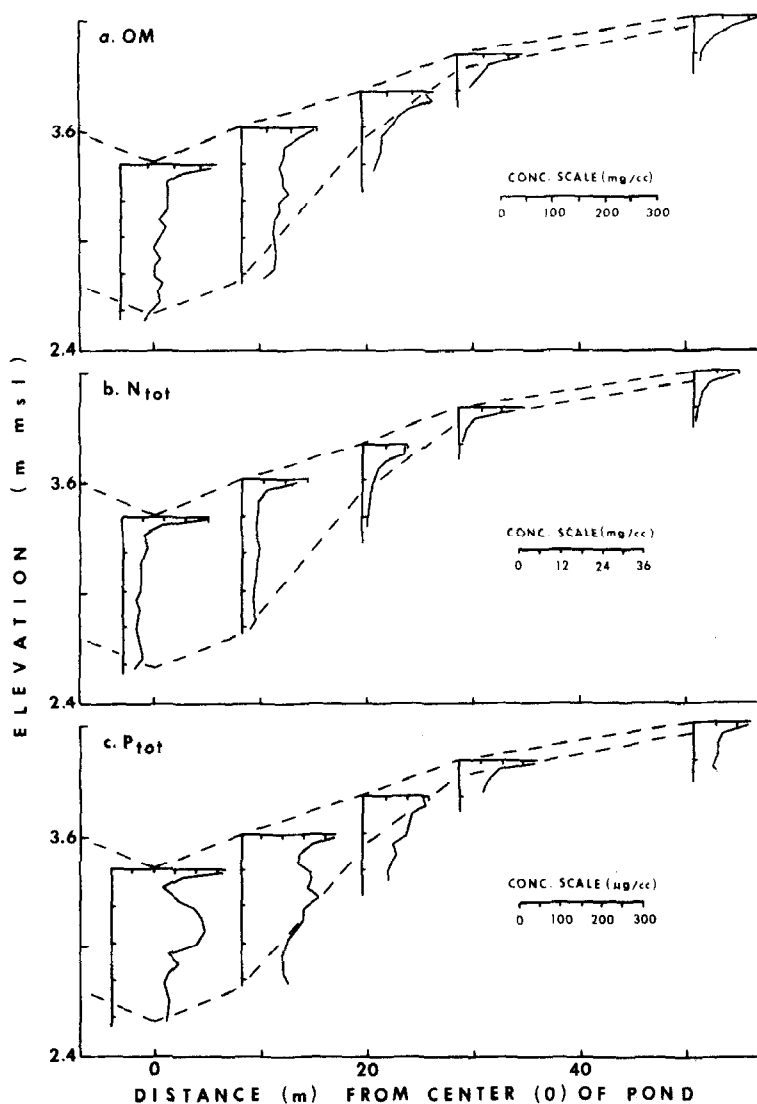


Figure 2. Distribution of nutrients in the pond sediments. The dashed lines show the sediments viewed in cross-section (bottom of the sediments was determined as stated in the text). The small graphs show the mean distribution of organic matter and nutrients from the center to the edge of the pond based on the sediment core data (see Figure 1 for areal location of cores). Seasonal low water was at 2.92 m msl in 1977 and at 3.63 in 1978. Y-axes off the distributional graphs correspond to the elevation data on the figure axes. Depth increments on the distributional graphs are 20 cm. (a) Organic matter distribution. X-axis increments on the distributional graphs are 50 mg cc^{-1} . (b) Total nitrogen distribution. X-axis increments are 6 mg cc^{-1} . (c) Total phosphorus distribution. X-axis increments are 50 µg cc^{-1} .

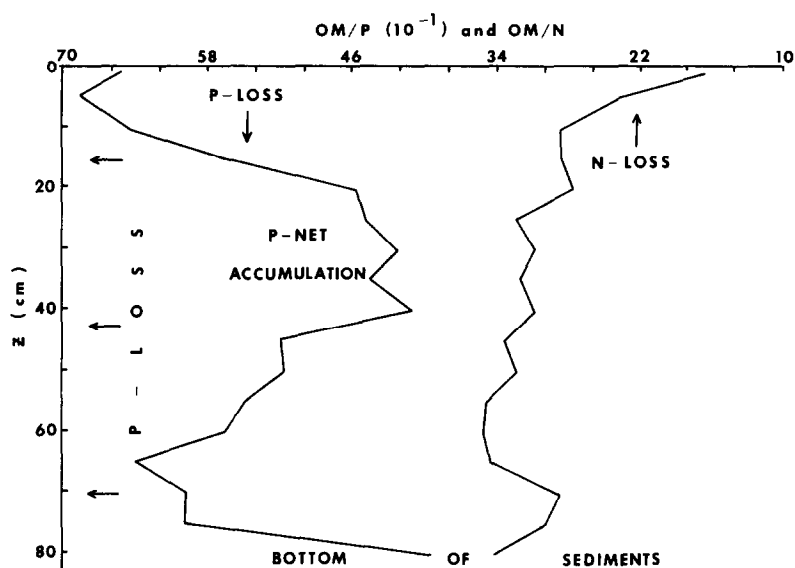


Figure 3. Mean OM/P and OM/N ratios plotted against depth in the sediments under a 200 m² circle at the center of the pond (see text for further explanation).

available for reuse in the water column. They will ultimately be released back to the atmosphere or lost from the system via the ground water, which will be tested later in the paper.

The pattern for phosphorus is different, however. After an initial decline in concentration in the top 10 cm at the center and out to the first concentric ring, TP concentration increases markedly to a depth of about 40 cm and then decreases to 120 mg cc⁻¹, remaining at that concentration to the bottom of sediments (Figure 2c). As with nitrogen, decomposition releases phosphorus; but since this nutrient has no gaseous component to its cycle it remains in the sediments. The apparent downward movement of P probably occurs during those dry seasons when the sediments are partially uncovered. As water is removed from the top layers of sediment by evaporation, phosphorus in solution is concentrated and moved downward by the evaporative water loss. Additionally, some available P may be leached downward by rainwater falling on the top of the uncovered sediments.

The functional dynamics of N and P can be more clearly understood by comparing their ratios to OM content. In Figure 3 the OM/P and OM/N ratios for the center and first concentric ring of cores have been averaged to show the fates of nitrogen and phosphorus under a 200 m² circular section at the center of the pond (Figure 1). The OM/P ratio decreases rapidly in the top 20 cm. This is due to the decomposition of organic matter and subsequent release of phosphorus. The available P is then

moved vertically in the sediments during the dry season by evaporation and percolation, as described above, resulting in the low OM/P ratios, that is, net P accumulation, between 20 and 40 cm. If the pond-water surface did not drop below the top of the sediments this available phosphorus should remain in place. Some phosphorus also moves laterally in the direction of mean water-table flow, as will be shown. The input from above, however, is sufficient to overcome this loss. Since the water table rarely drops below 40 cm, groundwater losses prevail below this level and the OM/P ratio increases. The bottom of the sediments is clearly delineated by a sharp decrease in the ratio as a result of a decline in organic matter content (Figure 2a) as the original sandy bottom of the depression is reached. This ratio is probably similar to that which would be found in the sandy flatwood soils surrounding the pond.

Sediment nitrogen dynamics is considerably different (Figure 3). High values of the OM/N ratio in the top portion of the sediments indicate that, since organic matter is not increasing with depth (Figure 2a), nitrogen is being removed at a more rapid rate than organic matter. In the early stages of diagenesis plant cell membranes break down, exposing the labile cellular constituents to chemical and biological activity (see, for example, Gjessing, 1976; Stevenson, 1982). A greater proportion of the total cellular nitrogenous constituents are in this labile form than are the other major components of organic matter, namely, carbon, oxygen, and hydrogen. Figure 2b shows that 75% of the total nitrogen at the top of the sediments is lost in the first 10 cm. After the initial increase, the OM/N ratio stabilizes indicating that all constituents of organic matter are being removed at roughly the same rate, albeit considerably more slowly than in the top 10 cm (Figure 2a, b).

Movement of nutrients in the ground water

Methods

Differences in the distribution patterns of the two nutrients should be reflected in the water table. Soluble phosphorus species should move laterally in the direction of mean water-table flow and show up as differences in concentration between upstream and downstream groundwater monitoring wells. Nitrogen, on the other hand, with its equilibrium relationship between sediments, water column, and, ultimately, the atmosphere, should exhibit a fairly constant concentration between groundwater inputs to and outputs from the pond.

To test this hypothesis the mean direction of lateral water-table flow was first determined by measuring groundwater heights in a series of observation wells. The slope of the groundwater surface is westerly in the direction of the discharge boundary, Myakkahatchee Creek, a tributary of

Table 1. Concentrations of total phosphorus and total nitrogen in water-table input and output wells¹

Date	\bar{x} P ($\mu\text{g l}^{-1}$)		\bar{x} N (mg l^{-1})	
	Input (E)	Output (W)	Input (E)	Output (W)
Apr 4	273 \pm 75	652 \pm 290	4.27 \pm 4.07	2.49 \pm 1.25
May 10	328 \pm 161(3)	753 \pm 110(2)	4.03 \pm 2.79	2.54 \pm 0.54(2)
Jun 7	383 \pm 150(3)	649 \pm 302(3)	3.10 \pm 1.71(3)	4.43 \pm 2.82(3)
Jul 6	160 \pm 46	258 \pm 137	1.43 \pm 0.56	1.32 \pm 0.09
Aug 4	81 \pm 13	156 \pm 62	1.36 \pm 0.20	1.50 \pm 0.30
Aug 30	87 \pm 26	285 \pm 224	1.33 \pm 0.17	1.39 \pm 0.21
Sep 28	98 \pm 19	244 \pm 275	1.16 \pm 0.42	1.77 \pm 0.41
Oct 27	38 \pm 17	169 \pm 113	1.00 \pm 0.28	1.78 \pm 0.64
Nov 21	91 \pm 42	161 \pm 137	1.41 \pm 0.36	1.98 \pm 0.46
Annual \bar{x}	171 \pm 125	370 \pm 242	2.12 \pm 1.30	2.13 \pm 0.97

¹ Each data point is the mean of four replicate wells except during the dry season (May and June) when some wells contained too little water to obtain a reliable sample. The number of replicates for these are in parentheses.

the Myakka River. Four replicate groundwater monitoring wells were placed on the eastern edge of the pond at 2 m intervals on a transect line perpendicular to an east-west line passing through center of the pond. Four replicate output monitoring wells were placed similarly on the western edge of the pond (Figure 1). Single wells were placed to the northwest and southwest of the pond center to ensure that any nutrient slug would not be missed (Figure 1). The positions of the wells correspond to the right edge of Figure 2. The bottoms of the wells were about 1.5 m below the ground surface and were screened to within 1 m of the ground surface. This placement allows for the sampling of that ground water which passes through the sediments at the center of the pond (Figure 2), and assuming little or no mixing of groundwater layers, the difference in nutrient concentration between input and output wells should reflect leaching losses from the sediments.

Groundwater samples were analyzed for TP using a persulfate digestion followed by the automated colorimetric ascorbic acid reduction method (EPA, 1974). Total kjeldahl nitrogen samples were digested with concentrated sulfuric acid and then measured by the automated selenium method; nitrate and nitrite were measured by the automated cadmium reduction method (EPA, 1974).

Results

Table 1 tends to confirm the conjecture about nutrient dynamics with respect to sediment/groundwater interaction. Greatly increased concentrations of phosphorus appear in the output wells for all dates whereas no such differences are apparent for nitrogen. The decline in concentration for both nutrients in all wells from spring to summer is the result of natural additions of relatively nutrient-poor precipitation on top of the water table

Table 2. Two-way analysis of variance with replication for groundwater concentrations of phosphorus and nitrogen

Source of variation	Total phosphorus			Total nitrogen		
	df	F	α	df	F	α
Wells	1,54	33.952	$\ll 0.001$	1,54	0.002	NS
Dates	8,54	12.524	$\ll 0.001$	8,54	4.312	< 0.001
Interaction	8,54	1.619	NS	8,54	1.089	NS

during the rainy season. Because of the mechanics of well sampling, the cone of depression that develops around a well in the process of pumping tends to reflect the average concentration from the bottom of the well to the top of the water table. When water levels are low the sampling process collects only the nutrient-rich waters that have passed through the sediments. When the water table is high this layer is sampled in addition to the nutrient-poor rainwater added to the top of the table.

total phosphorus concentrations do not differ across the pond is much less than 0.1% (Table 2). For total nitrogen there is no difference between input and output means. The hydrologic phenomena, discussed above, are illustrated by the variation between dates. The interaction variation, as expected, is insignificant indicating that time and concentration are not synergistically linked.

It is now possible to estimate the amount of phosphorus that is lost from the pond during the year and relate this to annual inputs. Phosphorus loss is the product of groundwater discharge through the pond and P concentration in this discharge minus background level, i.e., input-well concentration. Discharge is a function of (a) the size of the planar section (groundwater front) passing in an east to west direction through that portion of the sediments containing elevated P concentrations; (b) head loss; and (c) permeability. The planar section is bounded on the bottom by the elevation of the deepest-lying sediments, 2.6 m above mean sea level (msl) (Figure 2), and on the top by mean annual water height at the center of the pond, which is 54 cm, or 3.96 m msl (Coleman, 1979). The planar section extends horizontally to that point where the well-defined sediment lens stops and the stratigraphic profile begins to resemble that of the surrounding soils. This extent is determined from Figure 2 to be 30 m either side of the centerline. At this distance P concentration profiles are similar to those at the outer edge of the pond. This determination is substantiated by the fact that mean P concentrations in the two satellite wells (denoted by y's in Figure 1), both approximately 35 m from the east-west centerline, are not significantly different from background levels of the input wells (Coleman, 1979). The movement of the planar section of the groundwater front with reference to Figure 2 is through the page.

The area of the planar section, is, therefore, equal to (3.96 m minus 2.60 m) multiplied by 30 m multiplied by 2, or 81.6 m². The average water-

table head loss across the pond during 1978 was 1.84 mm m^{-1} (Coleman, 1979) and the permeability, $3.66 \text{ m}^3 \text{ day}^{-1} \text{ m}^{-2}$ (USDA, National Co-operative Soil Survey, 1977 and field inspection by the regional soil scientist). Annual discharge can now be calculated by Darcy's Law:

$$Q = PIA \times 365 \text{ days yr}^{-1}$$

where Q = Discharge ($\text{m}^3 \text{ yr}^{-1}$)

P = Permeability ($\text{m}^3 \text{ day}^{-1} \text{ m}^{-2}$)

I = Head loss (m m^{-1})

A = Area of the planar section (m^2).

The annual surplus-phosphorus-bearing water-table discharge across the pond is about 200 m^3 .

The mean concentration of surplus phosphorus at the centerline (the line passing through the east and west wells and the center of the pond) is about $200 \mu\text{g l}^{-1}$. At 30 m either side of the centerline, output P concentrations are assumed to be no different than background input levels, as discussed above. Assuming a constant rate of change in surplus phosphorus from the high concentrations at the centerline to zero at 30 m, the average surplus concentration in the groundwater front is 100 mg m^{-3} . This concentration multiplied by the annual discharge yields an annual loss estimate of 20 g yr^{-1} , with a 95% confidence range of 16 to 24 g yr^{-1} . Coleman (in press), in a paper which addresses the 5,000-year historical phosphorus budget of the pond, reports that the annual modern atmospheric input of P to the pond is 122 g yr^{-1} . The net loss to groundwater is, therefore, 16% of atmospheric input annually.

Discussion

The phosphorus and nitrogen nutrient cycles for the pond system are apparently fairly simple. Given the flat terrain and relatively porous surrounding soils, runoff inputs are considered to be negligible. Aside from unknown, and presumed small, biotic inputs to the pond, and the background levels in the water table, the atmosphere is the only significant source of phosphorus and nitrogen for the pond system. After some indeterminate residence time in the water column, where they are utilized by aquatic organisms, these nutrients become incorporated into the sediments. In the case of nitrogen, since there is no significant difference between input- and output-well concentrations, there is no substantial leakage to the water table. The processes of diagenesis apparently result in a physical and chemical balance between the sediments and the atmosphere, in effect, a closed cycle. The governor on the rate of nitrogen return from the sediments to the water column, and ultimately to the atmosphere, is the rate of organic matter decomposition in the sediments.

Phosphorus, on the other hand, presents quite a different picture. The top of the sediments probably decomposes fairly rapidly when uncovered during the dryer dry seasons. The unbound P travels vertically at first, as evaporation lowers the water table and the first rains of the next wet season percolate through the uncovered top of the sediments, removing any remaining available P. Upon reaching the top of the water table, the available phosphorus moves laterally along the groundwater gradient. As was the case with nitrogen, the rate of release from the sediments is a direct function of organic matter decomposition but the rate of movement out of the pond system is governed by the geophysical parameters of the system. Groundwater velocity is a function of gradient, permeability, and porosity, since the water only travels through the pores (see, for example, Domenico, 1972). In the case of the study pond the velocity is exceedingly slow because the water-table gradient is barely perceptible, only a couple of millimeters per meter. As a result phosphorus released from the sediments travels horizontally at about 6.8 m yr^{-1} (calculated from gradient and permeability values discussed earlier in the paper, and porosity of 36%, as determined by Coleman, 1979). At that rate phosphorus leaving the center of the pond will take nearly 7.5 years to reach the western edge of the pond, and the groundwater monitoring wells located there.

The nutrient dynamics determined for the study pond are probably directly applicable to other shallow lacustrine systems, as well as marshes, in similar substrates, where water-table fluctuations routinely uncover portions of the sediments, particularly on the Coastal Plain of the United States. It should be noted that phosphorus transfer may be considerably more rapid in some of these systems if the groundwater gradient is substantial or if they are located in highly permeable substrates.

As to the applicability to deep-water lakes where oxidation of the sediments is very slow, the pond may serve as a laboratory analog where the time factor has been accelerated. In other words, all lacustrine systems probably lose some phosphorus via the ground water as a result of diagenetic processes and horizontal or vertical leaching. The rate of loss is governed first by the sediment release rate and secondly by the intrinsic geophysical characteristics of the system.

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