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MINERAL FLUX IN THE BONEY MARSH, KISSIMMEE RIVER

1. MINERAL RETENTION IN RELATION TO OVERLAND FLOW DURING THE THREE-YEAR PERIOD FOLLOWING REFLOODING

By

Steven M. Davis

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Resource Planning Department
South Florida Water Management District
West Palm Beach, Florida

FOREWARD

This report is the first of a series on mineral flux in the Boney Marsh experimental area on the Kissimmee River floodplain. The Boney Marsh study was undertaken to provide basic information about marsh mineral cycling which is prerequisite to evaluating the water quality benefits from various river restoration proposals. This report focuses on reductions in mineral concentrations between river inflows and outflows and on mineral budgets, considering all inputs and outputs, for the Boney Marsh during three years following its construction and reflooding. Two additional communications are planned. A second report will provide estimates of mineral flux in the marsh vegetation during annual cycles of growth, mortality and decomposition. A third will elucidate successional trends in species composition, standing crop, and mineral storage of the marsh vegetation. Relationships between plant succession and mineral retention by the marsh will be examined. Management implications to be drawn from the completed sequence of studies include: (1) comparison of the effectiveness of overland flow vs water level fluctuation as means of improving river water quality, (2) estimation of the areas of marsh required to significantly improve river water quality using the overland flow and water level fluctuation strategies, and (3) prediction of the period of time after reflooding that a marsh area will remain effective in mineral removal under given conditions of hydroperiod, water flow, and mineral supply.

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ABSTRACT

This study investigated mineral retention by a Kissimmee River marsh during a three-year period following reflooding. The marsh was divided into flow-thru and no-flow areas for the purpose of assessing how overland flow augmented mineral retention. Reductions in mineral concentrations in river water flowing across the flow-thru marsh were estimated. Mineral budgets for both marsh areas were provided based on all inputs and outputs.

Both marsh areas acted as year-round sinks for phosphorus and nitrogen. River water was the main input of phosphorus and nitrogen to the flow-thru marsh, while rainfall supplied most of these elements to the no-flow marsh. Overland flow increased annual supplies of phosphorus and nitrogen and resulted in a larger retention of these elements by the flow-thru marsh. However, the no-flow marsh retained a larger proportion of the limited phosphorus and nitrogen inputs which it received through rainfall and water level fluctuations.

INTRODUCTION

From its headwaters in Lake Kissimmee, the Kissimmee River in its natural state meandered extensively across a 1.6 km wide floodplain of marshes and oxbows as it flowed toward Lake Okeechobee about 80 km to the south. River stages fluctuated widely, generally rising during the June-October wet period and declining during the November-May dry period. The irregularity of the river slowed water flows in the channel, forcing floodwater across the extensive floodplain marsh enroute to Lake Okeechobee. Channelization of the river with the construction of C-38 in the 1960's reduced the marshes on the mainstream floodplain to relatively small pools at the lower ends of five impoundments. Water level fluctuations and the flow of water over the floodplain were largely eliminated.

The Kissimmee River is a major contributor of phosphorus and nitrogen to Lake Okeechobee (Davis and Marshall, 1975). The river supplied 22% of the phosphorus inflow and 27% of the nitrogen inflow into Lake Okeechobee during 1973-1978 (Dickson et al., 1978). However, this nutrient contribution was attributed to the large discharge of the river rather than to poor water quality. Davis and Marshall found that average phosphorus concentrations of .084 mg/l and nitrogen concentrations of 1.39 mg/l in the Kissimmee River water entering Lake Okeechobee were lower than those of any inflows other than rainfall. Jones and Lee (1978) estimated that a 50% reduction in the already low phosphorus concentration in the river water would be required to noticeably reduce chlorophyll _a_ concentrations in Lake Okeechobee. The reduction of phosphorus levels in Kissimmee River water has been an important justification for the numerous proposals for restoring the river and floodplain to a more natural state (McCaffrey et al., 1977).

Most of these proposals can be grouped into two basic approaches. One approach involves the restoration of an annual water level fluctuation in each of the river's impoundments by raising and lowering the outflow gates of the existing structures. This alternative would expand the marsh areas in each impoundment into higher contours and would provide these marshes with a relatively natural wet-dry season water regime. The other approach involves routing the flow of water down the original river channel and over portions of the floodplain rather than allowing the water to flow directly down C-38. Methods to accomplish this include plugging C-38 or filling in the entire canal. The benefits to fish and wildlife of restoring water level fluctuations to the floodplain already have been well documented (Dineen et al., 1974; Goodrick and Milleson, 1974; Milleson, 1976). Water quality improvements resulting from water level fluctuation and additional benefits which might result from the creation of overland flow have not previously been quantitatively evaluated. The purpose of this study is to estimate the capability of a Kissimmee River marsh to remove nutrients from the river water and to determine the extent to which overland flow augments this capability. The two basic restoration schemes of water fluctuation and overland flow are simulated and compared.

STUDY AREA

The Boney Marsh (Figure 1) is a 142 ha diked experimental marsh area in which water inflows and stages are controlled and monitored. The area is located on the Kissimmee River floodplain in Pool B, the second impoundment south of Lake Kissimmee in Highlands County, FL. The marsh was originally diked and drained for pasture in 1963 and was reflooded in 1966 after the Central and Southern Florida Flood Control District acquired the land. Water levels were kept well below the ground surface throughout the majority of 1975 during the construction of the experimental area. The area was reflooded in November 1975 upon completion of construction. Vegetation within the marsh during this study consisted largely of a mixture of *Panicum hemitomon*, *Pontederia lanceolata*, *Sagittaria lancifolia*, *Panicum repens*, *Cephalanthus occidentalis*, *Bacopa caroliniana*, *Hydrochloa carolinensis*, and *Eleocharis acicularis*. The latter 3 species became less abundant the first year after reflooding. A floating mat of *Scirpus cubensis* covered a 16 ha depression in the SE corner of the area, and a 3-ha stand of *Salix caroliniana* grew just to the N of this depression.

An annually fluctuating water regime resembling average conditions before channelization was maintained in the area. This water regime was based on mean monthly river stages at Fort Kissimmee from 1941 to 1958. Elevation differences between Fort Kissimmee and the Boney Marsh were applied to Fort Kissimmee mean monthly stages to approximate corresponding stages in the experimental area. These stages ranged from 39.7 to 42.7 ft (12.11 - 13.02 m) msl. The monthly stages to be maintained in the experiment were lowered 0.7 ft (0.21 m) in order to contain the water below the 42 ft (12.81 m) contour and to lower water levels to near the ground surface during spring. This resulted in an annual water level

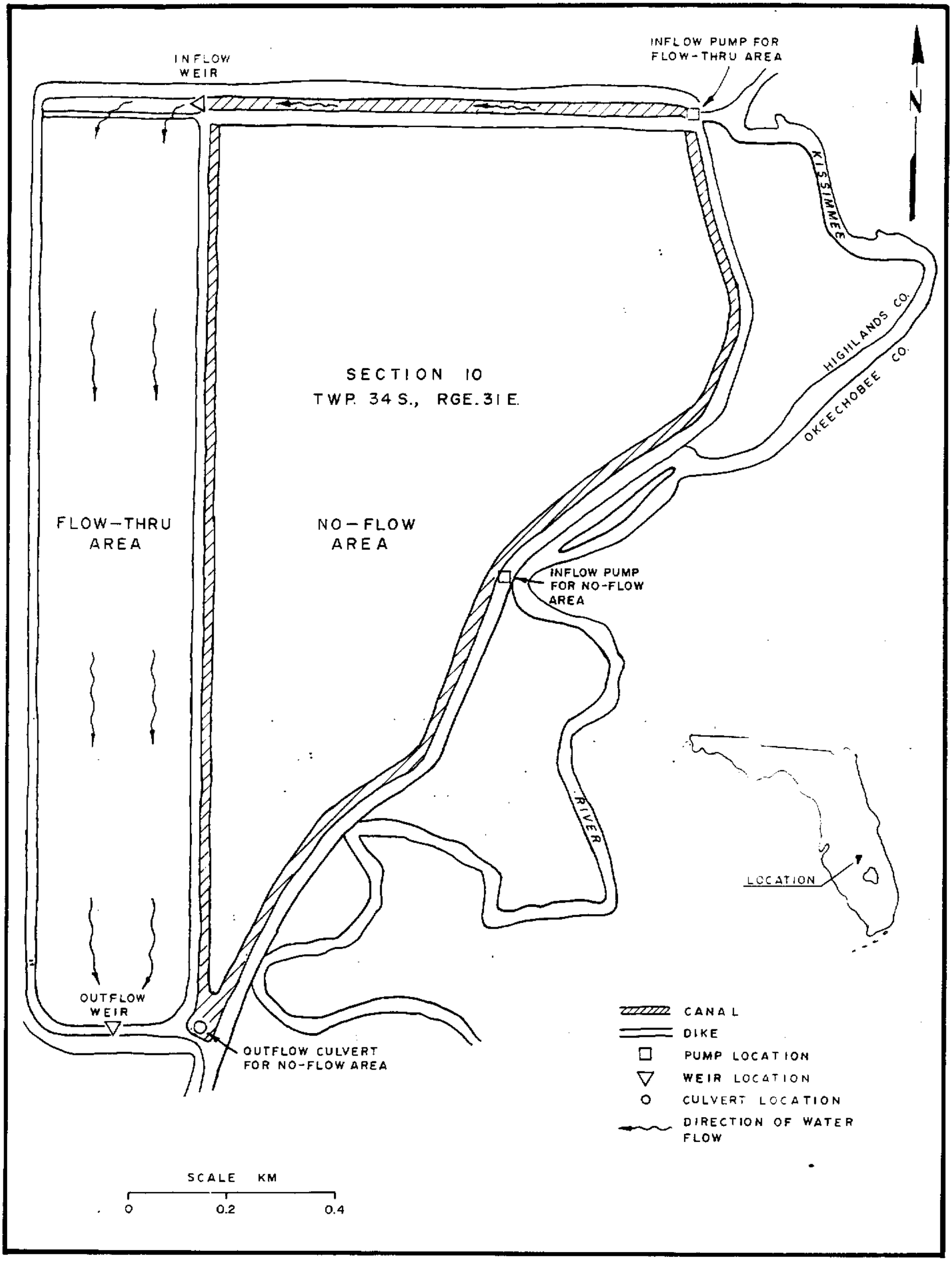

FIG. 1 Boney Marsh Experimental Area

fluctuation of 39.0 to 42.0 ft (11.90 - 12.81 m) msl in the area. To maintain this water regime, the water elevation upstream of the outflow weir and culvert was adjusted approximately as follows:

	Approx. Elev. MSL	
Date	Feet	Meters
1 February	39.7	12.11
1 May	39.0	11.90
15 June	39.7	12.11
1 August	40.3	12.29
1 September	41.0	12.50
1 October	42.0	12.81
1 November	41.0	12.50
1 December	40.3	12.29

The experimental area was divided into two parts. One area was subjected to nearly continuous overland flow of pumped river water. The other area was subjected to more stagnant conditions with flow resulting primarily from rainfall and from infrequent pumping of river water to maintain the water fluctuation schedule. The continuous flow treatment was applied to a strip of marsh 48.6 ha in area and 1.61 km in length in the western section of the experimental area. Pumped river water flowed across this section five days per week during the 46 weeks when the stage was maintained at or above 39.7 ft msl. No water flow was supplied to this area during the 1 May to 15 June low-water period when the stage was dropped to 39 ft msl. The no-flow treatment was applied to a 93.1 ha area of marsh in the eastern section only as necessary to maintain the annually fluctuating water regulation schedule.

METHODS

Water samples were collected from each inflow and outflow daily on Monday-Friday between March 1976 and March 1979. Rainfall was collected daily at S-65B approximately 3.2 km south of the experimental area. Water samples were refrigerated shortly after collection. The water samples were combined into weekly composite samples for each inflow and outflow and for rainfall. The weekly composite samples were analyzed for phosphorus and nitrogen (dissolved inorganic, dissolved organic, and particulate) and for potassium, calcium, magnesium, sodium, and chloride. Samples to be analyzed for dissolved minerals were filtered through 0.45 micron nucleopore filters. Differences in mineral concentration between inflows and outflows were tested statistically by applying paired t tests to the weekly sets of values for each year.

Water samples were collected at 0.16 km intervals along the length of the flow-thru marsh between inflow and outflow points to provide profiles indicating the portion of the marsh where mineral concentrations decreased. Each distance from the inflow was sampled at locations about 30 m inside the east and west dikes. Chemical concentrations in those two samples were averaged. The profile samples were analyzed for those parameters which were found to differ significantly between inflows and outflows. Profile samples were collected monthly from April 1978 to March 1979. Temporal variations in the profiles from month to month did not show distinct seasonal patterns, so the monthly data were averaged to provide annual profiles.

Analyses were performed by the South Florida Water Management District Water Chemistry Laboratory. Samples for total and total dissolved phosphorus analyses were digested using an autoclave. Samples for total and total dissolved nitrogen analyses were digested by the Kjeldahl procedure using a block digester. Analyses for phosphorus and nitrogen were made using a Technicon Auto-Analyzer II$^{(R)}$. Cation analyses were made using a Perkin-Elmer 306 Atomic Absorption Spectrophotometer. When the concentration of a chemical parameter fell below the detection limit of the chemistry lab, the detection limit was used as the concentration. Details of analysis procedures are presented in Appendix A.

Water budgets for the flow-thru and no-flow marshes were determined by Trimble and Mireau (1980). Weekly rainfall amounts and water discharges into and out of the marshes were derived from the water budgets. Mineral inputs and outputs were estimated by multiplying the water inflows, outflows, and rainfall amounts by the mineral concentrations in the water.

HYDROLOGY

The water budgets of the flow-thru and no-flow marshes differed in the total water supply per hectare of the marsh and in the relative contribution of rainfall and pumped river water to this supply. Water inputs and losses are summarized from Trimble and Mierau (1980) in Table 1. The annual water supply in $m^3/ha^{(1)}$ to the flow-thru marsh was 5.3 to 6.2 times the supply to the no-flow marsh. The combined rainfall and pumped water input to the flow-thru area varied annually from 107,360 to 111,210 m^3/ha while the annual water input to the no-flow marsh totalled only 17,780 - 20,940 m^3/ha. The larger water input to the flow-thru marsh resulted from the daily pumping of river water into this area the majority of the year. Pumped river water was the major water source for the flow-thru marsh, making up 87-92% of the annual water supplies to this area. Rainfall supplied a relatively small proportion (9-13%) of the water input to the flow-thru marsh. Rainfall and pumped river water were about equally important as water sources for the no-flow marsh; rainfall provided 45-69% of the annual water supplies to this area.

Rainfall contributed between 8,860 and 14,530 m^3/ha of water annually to each marsh area (Table 1). Precipitation generally followed a seasonal pattern of a June-November rainy period and a December-May dry period; however, this varied from year to year. Particularly heavy rains during summer 1978 substantially increased annual precipitation during the third year of the study. Evapotranspiration rates of 13,200 to 13,580 $m^3/ha/yr$ remained relatively constant from year to year, exceeding rainfall during the first two years of the study but not during the third (Table 1). The seasonal pattern of ET was consistent from year to year, with maximum

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$^{(1)}$1 $m^3/ha \simeq 14.3$ cu.ft./acre

TABLE 1. WATER INPUTS AND LOSSES (m^3 X 1000/ha) IN BONEY MARSH, KISSIMMEE RIVER.

		FLOW-THRU MARSH				NO-FLOW MARSH			
		Rain	Inflow	Outflow	ET	Rain	Inflow	Outflow	ET
1976-77	Spring	2.34	20.40	18.73	4.17	2.34	0.00	0.18	4.17
	Summer	4.10	22.49	17.49	4.06	4.10	2.50	0.59	4.06
	Autumn	1.85	32.93	30.14	3.07	1.85	5.56	1.11	3.07
	Winter	1.29	23.93	23.14	2.04	1.29	0.14	1.33	2.04
	TOTAL	9.58	99.75	89.50	13.34	9.58	8.20	3.21	13.34
1977-78	Spring	1.31	27.17	22.17	4.50	1.31	1.16	0.68	4.50
	Summer	2.58	16.65	11.19	4.12	2.58	3.99	1.22	4.12
	Autumn	2.64	25.25	29.53	3.08	2.64	5.78	1.30	3.08
	Winter	2.33	29.43	29.82	1.88	2.33	0.00	0.98	1.88
	TOTAL	8.86	98.50	92.71	13.58	8.86	10.93	4.18	13.58
1978-79	Spring	1.92	24.68	19.48	4.02	1.92	0.69	1.06	4.02
	Summer	7.25	21.96	23.16	3.90	7.25	0.74	0.38	3.90
	Autumn	2.79	23.44	29.25	3.09	2.79	4.61	4.17	3.09
	Winter	2.57	26.60	32.31	2.19	2.57	0.37	1.81	2.19
	TOTAL	14.53	96.68	104.20	13.20	14.53	6.41	7.42	13.20

values during the warm, dry spring months and minimum values during the winter. The pumped inflow of river water into the flow-thru marsh varied from 96,680 to 99,750 m^3/ha each year, while annual outflows from this area ranged from 89,500 - 104,200 m^3/ha (Table 1). The no-flow marsh received pumped river water inflows of 6,410 to 10,930 m^3/ha annually (Table 1). Water was pumped into this area primarily during September and October each year in order to raise water stages to their annual maximum in October. Water outflows from this area totalled 3,210 and 4,180 m^3/ha during the first two years of the study. Heavier rainfall during the third year increased the water outflow from the no-flow marsh to 7,420 m^3/ha.

PHOSPHORUS

Previous Work

Several nutrient uptake studies in freshwater wetlands have demonstrated reductions in phosphorus concentrations between inflows and outflows (Table 2). Comparison of these studies indicates that both the magnitude and percent efficiency of phosphorus uptake by freshwater wetlands may be related to inflow concentrations. Reductions in phosphorus concentration of 95-98% have been reported primarily where inflows of wastewater plant effluent contained between three and 11 mg P/l in Bellaire Wetland in Michigan (Kadlec and Tilton, 1978), Brookhaven meadow-marsh systems in N.Y. (Small, 1978), Lake Balaton in Hungary (Toth, 1972), and a central Florida hardwood swamp/marsh (Boyt et al., 1977). Smaller reductions of 16-60% have been reported for wetlands receiving inflow phosphorus concentrations $\leq$ 2 mg/l. Examples include Horicon Marsh in Wisconsin (Bentley, 1969), Theresa Marsh in Wisconsin (Klopatek, 1975), Santee Swamp in South Carolina (Kitchens et al., 1975), Chandler Slough in Florida (Federico et al., 1978) and the reed zone of Bodensee, formerly Lake Constance, in Germany-Switzerland (Banoub, 1975).

In spite of these demonstrations of reductions in phosphorus concentration of surface waters by wetlands, confusion still exists concerning the value of wetlands as a nutrient sink. This confusion results partially from an inadequate understanding of phosphorus release by wetlands. Lee et al. (1975) concluded that most of the phosphorus removed from inflowing water by Wisconsin marshes during the summer was released during the following spring thaw. The drainage of these marshes also resulted in a significant release of phosphorus from the marsh soils due to the solubilization of particulate organic forms, eliminating the beneficial effects of the marshes on water quality. Federico et al. (1978) reported a large phosphorus loss from Chandler Slough, Florida, with the "first flush" from summer rains. This "first flush" followed the winter period of reduced plant growth as well as the late winter-spring dry season.

Another source of confusion regarding wetlands as nutrient sinks has been the paucity of information about their phosphorus budgets. The majority of estimates of phosphorus uptake by wetlands have been based on inflow and outflow concentrations rather than on mass balances of all inputs and outputs. Much of the difficulty in calculating phosphorus budgets of wetlands arises from their complex hydrology. Few natural marshes are amenable to the accurate measurements of surface water inflows and outflows, rainfall, evapotranspiration, and groundwater seepage, all of which contribute to the mass balance of phosphorus. The phosphorus budgets which have been constructed for freshwater wetlands suggest that these wetlands can act as phosphorus sinks. Mitsch et al. (1979) constructed a phosphorus budget for a southern Illinois cypress swamp in which total annual inputs of 3.85 g/m^2, resulting primarily from deposition of high phosphorus sediments during flooding of the Cache River, were reduced about 90% in the outflows. Similar results were reported by Boyt et al. (1977) for a combined hardwood swamp and marsh in central Florida; their phosphorus budget showed a total export from the swamp of 0.115 g P/m^2/yr, which was only 13% of the total influx. Dolan (1978) constructed a phosphorus budget for Clermont Marsh in central Florida where 34 g P/m^2 was applied in sewage effluent over a 10.5 month period, while less than one g P/m^2 exited primarily through groundwater flow. The Clermont Marsh study differed from the other work cited in that the water table remained below the soil surface during most of the year.

TABLE 2. REDUCTION IN TOTAL P CONCENTRATIONS (MG/L) OF SURFACE WATER BY WETLANDS

LOCATION	INFLOW	OUTFLOW	% REDUCTION	SOURCE
Meadow-marsh models, Brookhaven, New York	$\leq$ 11.0	< 2.0	-	Small (1978)
Central Florida hardwood swamp	6.4	< 1.0	98%	Boyt et al (1977)
Lake Balaton reed zone, Hungary[2]	5.56	0.091	98%	Toth (1972)
Bellaire Wetland, Michigan	3.48	0.11	97%	Kadlec and Tilton (1978)
Horicon Marsh, Wisconsin (winter)	2.00	1.00	50%	Bentley (1969)
Houghton Lake Wetland, Michigan	0.41	0.05	95%	Kadlec and Tilton (1978)
Santee Swamp, South Carolina	0.182-.875	-	50%	Kitchens et al (1975)
Theresa Marsh, Wisconsin	0.10-0.78	0.10-0.50	50%[1]	Klopatek (1975)
Horicon Marsh, Wisconsin (summer)	0.31	0.13	58%	Bentley (1969)
Chandler Slough, Florida, 1976	.349	.226	35%	Federico et al (1978)
Chandler Slough, Florida, 1975	.276	.232	16%	Federico et al (1978)
Bodensee reed zone, Germany-Switzerland	.046	.033	28%	Banoub (1975)

[1]When compared to Cl

[2]Mean reductions in P concentrations from 2 sewage purification plants during July and August

Rainfall as a source of phosphorus to wetlands has been largely ignored in most of the phosphorus uptake studies which have been based on inflow-outflow concentrations rather than on mass balances. The few studies which have been done on rainfall phosphorus suggest that this may be an important input in the phosphorus mass balances of marshes. Likens (1975) estimated the average quantity of phosphorus in rainfall from various sources to be 0.030 $g/m^2/yr$. A similar annual phosphorus supply from rain of 0.027 $g/m^2/yr$ was reported by Gore (1968) for the period of 1959-1965 near Moor House, England. Reimold and Daiber (1967) illustrated that rainfall phosphorus can influence the quality of surface water; seasonal fluctuations of phosphorus in rain from .152 mg/l during winter-spring to $\geq$4.646 mg/l during summer caused an atypical seasonal phosphorus cycle in a Delaware estuary.

Concentrations of phosphorus in Florida rainfall have been fairly well documented. Brezonik and Shannon (1971) calculated that rain contributed between 26 and 59% of the phosphorus supply to some north central Florida lakes. These calculations were based on an average concentration of 0.033 mg/l total P in rainfall at Anderson - Cue and McCloud Lakes near Gainesville, Florida, (Brezonik et al., 1969). Brezonik (1973) pointed out that rainfall ortho-PO_4 concentrations of 0.06 - 0.40 mg P/l near Gainesville during the summer of 1968 were, with few exceptions, higher than the critical concentrations of 0.01 mg/l said to stimulate algal blooms in lakes. Rainfall during the same period over a more rural area near Cedar Key, Florida, contained lower ortho-PO_4 concentrations of .007 to .036 mg P/l and showed no trends with distance from the coast (Brezonik, 1973). Shannon (1978) reported concentrations of total P between .050 and .090 mg/l in precipitation at three agricultural sites in South Florida. Comparison of Brezonik's Gainesville and

Cedar Key data and Shannon's agricultural site data suggests that urban rainfall may contain more phosphorus than rural rainfall and that agriculture may increase the phosphorus content of rural rainfall in Florida.

In summary, the literature to date indicates that freshwater marshes can reduce phosphorus concentrations in surface water; however, uptake may be less efficient when inflow concentrations are low. Significant phosphorus releases from marshes may occur during winter periods of plant dieback and following the drainage of marsh soils. Most of the previous research on marsh phosphorus uptake has been done in temperate latitudes; marsh phosphorus uptake is poorly documented in subtropical and tropical latitudes, where winter and summer seasonal extremes in temperature are replaced by wet season and dry season rainfall patterns. The majority of uptake studies, which are based on phosphorus concentrations in inflowing and outflowing waters, probably under-estimate phosphorus retention since they ignore phosphorus inputs through rainfall and the concentration of phosphorus in marsh water due to evapotranspiration. The supply of phosphorus through rainfall has been shown to be significant. The few mass balances of phosphorus which have been constructed for freshwater wetlands indicate that swamps and marshes can act as year-round sinks for phosphorus. This study reports inflow-outflow phosphorus concentrations as well as mass balances for a subtropical marsh which received river water containing phosphorus concentrations <0.1 mg/l.

Results

Phosphorus Concentration in Water

Phosphorus concentrations in river inflows to the flow-thru marsh were consistently higher than those in outflows (Figure 2). The phosphorus concentration in inflowing water peaked during late summer or fall each year. These peaks resulted from increases in particulate P during the first year and from increases in dissolved P during the latter two years. The short duration, large magnitude and predominance of particulate P during the 1976 summer peak suggest that this increase resulted from a plankton bloom in the inflowing river water. The high particulate P concentrations in inflowing water during summer 1976 were not reduced as the water flowed over the marsh, the outflow values being nearly as high as the inflow values. The summer-fall increases in dissolved phosphorus during the last two years were effectively reduced 86 and 77% by the flow-thru marsh.

The annual reductions in phosphorus concentrations between the river inflows and the marsh outflows of the flow-thru area were significant ($p = 0.05$) each year of the study (Table 3). While the mean concentrations of total P in the inflowing water increased from year to year, concentrations in outflowing water decreased. Thus the marsh became progressively more efficient in reducing phosphorus concentration. Inflow total P concentrations of .035, .045 and .047 mg/l averaged annually were reduced 37, 53, and 64% respectively during the first, second and third years of the study. Dissolved inorganic P concentrations were reduced 62-77% each year between the inflow and outflow of the flow-thru marsh, while dissolved organic P concentrations were lowered 46-65%. Lesser reductions occurred in particulate P, and these were statistically significant only during the last year.

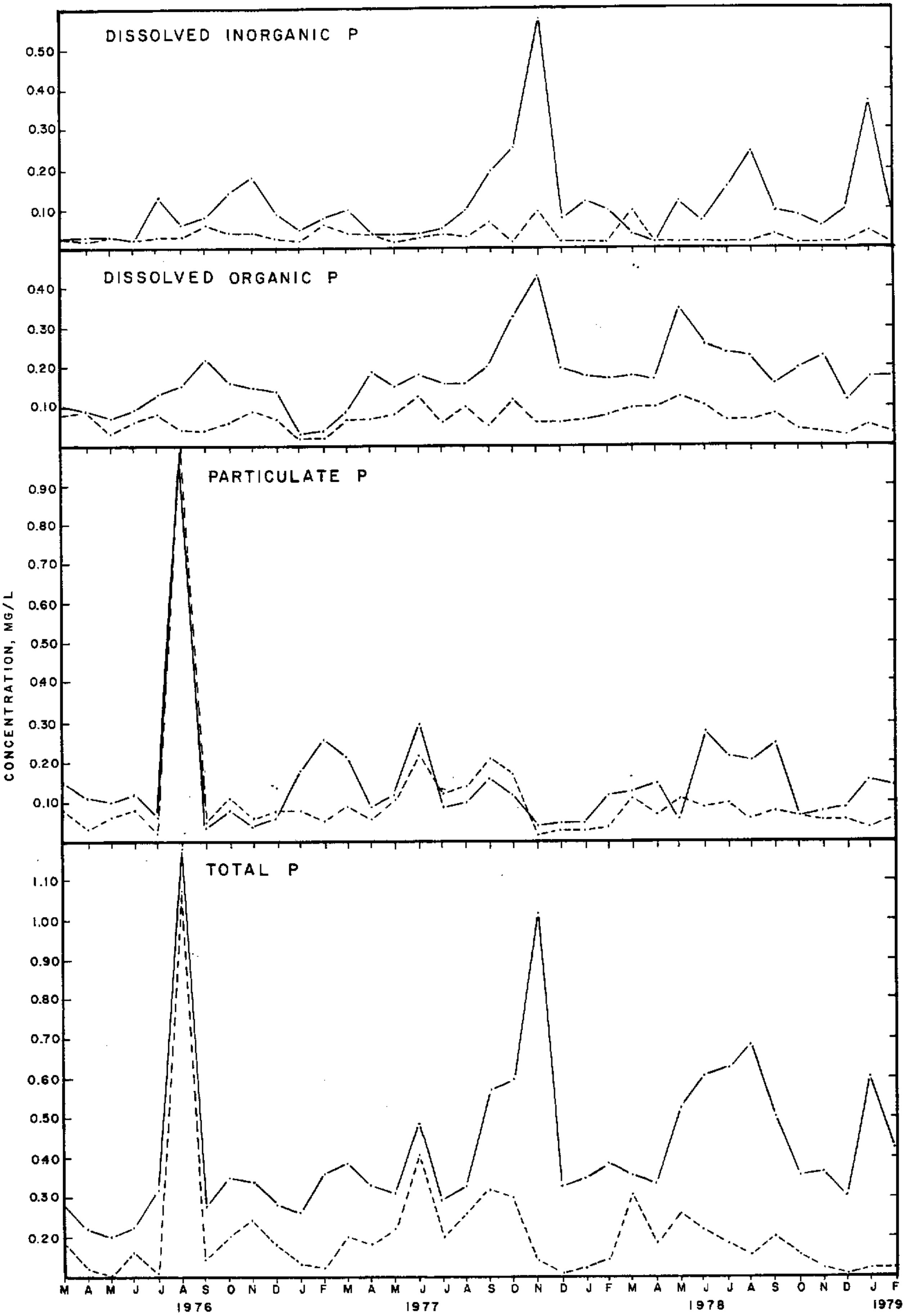

FIG. 2 Monthly average phosphorus concentrations in inflow (solid line) and outflow (dashed line) water of flow-thru marsh.

TABLE 3. AVERAGE MINERAL CONCENTRATIONS (mg/l) IN THE WATER INFLOWS AND OUTFLOWS OF THE FLOW-THRU MARSH. ASTERISKS INDICATE THAT INFLOW AND OUTFLOW CONCENTRATIONS WERE SIGNIFICANTLY DIFFERENT AT THE 95% CONFIDENCE LEVEL.

	March 76-77			March 77-78			March 78-79		
	IN	OUT		IN	OUT		IN	OUT	
PHOSPHORUS									
Dissolved Inorganic	.008	.003	*	.015	.004	*	.013	.003	*
Dissolved Organic	.011	.006	*	.020	.007	*	.020	.007	*
Particulate	.018	.014		.011	.010		.016	.007	*
Total	.035	.022	*	.045	.021	*	.047	.017	*
NITROGEN									
Dissolved Inorganic	0.12	0.07	*	0.09	0.03	*	0.08	0.03	*
Dissolved Organic	0.95	0.99		1.16	1.20		1.29	1.31	
Particulate	0.34	0.27		0.30	0.28		0.21	0.25	
Total	1.36	1.32		1.46	1.42		1.47	1.47	
SODIUM	8.78	8.32		9.88	10.31		7.43	7.50	
POTASSIUM	0.90	0.63	*	1.30	1.04	*	0.97	0.85	
CALCIUM	11.49	10.95		13.43	13.10		11.31	11.83	
MAGNESIUM	2.21	1.99	*	2.85	2.92		2.04	2.04	
CHLORIDE	-	-		17.6	17.6		12.8	12.1	*

Most of the decrease in phosphorus concentration of the river water which entered the flow-thru marsh occurred in the upper 0.64 km length of the marsh (Figure 3) in an area encompassing about 19.4 ha. Eighty-eight percent of the total P reduction between inflow and outflow took place in this upstream reach. Reductions of dissolved inorganic P, dissolved organic P and particulate P in the upper 0.64 km amounted to 100%, 71%, and 100% of their total decreases between inflow and outflow points. Particulate P appeared to increase slightly and then decrease again as the water flowed through the downstream half of the flow-thru marsh.

Phosphorus concentrations in rainfall fluctuated widely from month to month. No seasonal pattern was evident in these fluctuations. Neither was there any apparent correlation between phosphorus concentration and rainfall amount on a weekly or monthly basis. Rainwater phosphorus

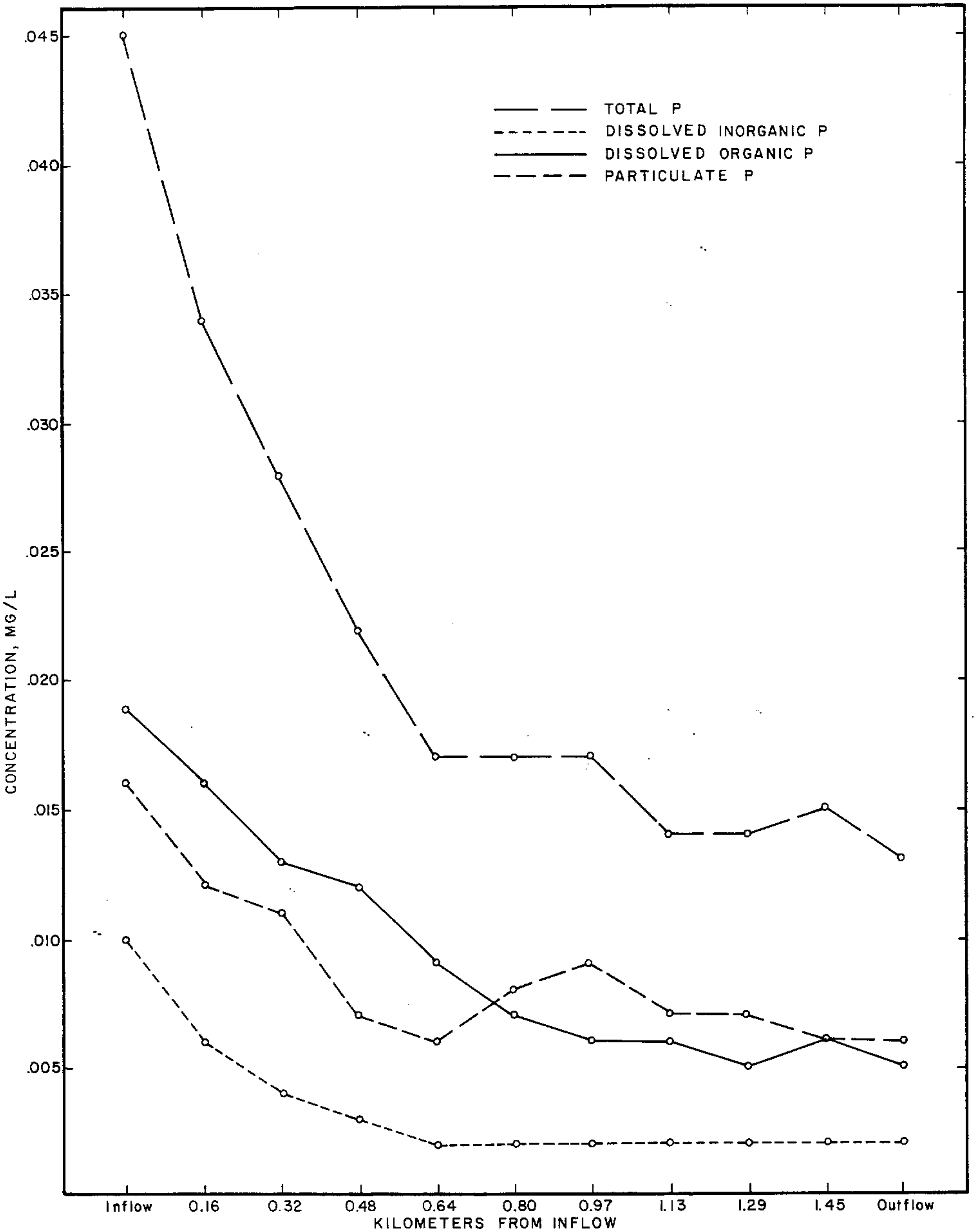

FIG. 3. Reductions in phosphorus concentrations in the water along the length of the flow-thru marsh.

concentrations were particularly high between October 1979 and May 1980. Rainwater differed markedly from the pumped river water inflows both in total phosphorus concentrations and in relative importance of the three phosphorus fractions. The total P concentration of .174 mg/l in rainfall exceeded the total concentration of .043 mg/l in river water by about fourfold when averaged over the three year study period (Table 4). Most of the rainwater phosphorus was dissolved inorganic. This fraction made up 75% of the total phosphorus in rainwater but only 27% of the total in river water. Most of the phosphorus in river water was dissolved organic or particulate. Each of these fractions made up 34-39% of the river water phosphorus and 12-13% of the rainwater phosphorus.

TABLE 4. MINERAL CONCENTRATIONS (mg/l) IN RAINFALL, RIVER INFLOWS AND MARSH OUTFLOWS AVERAGED OVER A THREE-YEAR PERIOD.

PHOSPHORUS	RAIN	RIVER INFLOW	FLOW-THRU OUTFLOW	NO-FLOW OUTFLOW
Dissolved Inorganic	.142	.012	.003	.010
Dissolved Organic	.023	.017	.007	.010
Particulate	.025	.015	.010	.010
Total	.174	.043	.020	.028
NITROGEN				
Dissolved Inorganic	.87	.09	.04	.07
Dissolved Organic	1.14	1.17	1.14	1.15
Particulate	.36	.27	.24	.31
Total	2.34	1.45	1.34	1.48
SODIUM	<2.99	8.71	8.54	9.33
POTASSIUM	.54	1.07	.83	.77
CALCIUM	<3.23	11.96	11.89	11.08
MAGNESIUM	<1.11	2.33	2.26	2.24
CHLORIDE	<4.27	15.04	14.40	14.87

Phosphorus concentrations in outflow water from the no-flow marsh exceeded those in the outflow from the flow-thru marsh (Table 4). The difference between the two outflows resulted primarily from dissolved inorganic P, which averaged over three times higher in outflow water from the no-flow marsh than in the outflow from the flow-thru marsh. This difference is attributed to the major source of water to each of these areas, rainfall for the no-flow marsh and river water for the flow-thru marsh. The higher phosphorus concentrations in rainfall compared to river water corresponded to the higher concentrations in outflows of the no-flow marsh compared to the flow-thru marsh.

Phosphorus Budgets

Even though most of the net reduction in phosphorus concentration occurred in the upstream 19.4 ha of the flow-thru marsh, the influx and outflux of phosphorus is expressed as kg/ha based on the total area of each marsh. It is assumed that both uptake and release of phosphorus occurred throughout the marsh and that the entire area was involved in the overall net retention of phosphorus each year.

Rainfall contributed most of the phosphorus supply to the no-flow marsh, river water inflow most to the flow-thru marsh (Table 5). Averaged over the three year study period, rain supplied 83% of the total P input to the no-flow marsh. This was the case also for each phosphorus fraction; 95% of the dissolved inorganic P, 64% of the dissolved organic P and 60% of the particulate P entering the no-flow area each year were supplied by rainfall. Rainfall was less important in the phosphorus budget of the flow-thru marsh, where 69% of the annual phosphorus supply was through the pumped inflow of river water. This pumped inflow provided 45% of the dissolved inorganic P, 87% of dissolved organic P and 84% of the particulate P to the flow-thru marsh each year. The relative importance of rainfall and pumped river water to the phosphorus budget of each marsh

TABLE 5. ANNUAL INFLUX AND OUTFLUX (g/ha/yr) OF PHOSPHORUS IN THE BONEY MARSH.

	FLOW-THRU MARSH				NO-FLOW MARSH			
	Rain	River Inflow	Total Inflow	Outflow	Rain	River Inflow	Total Inflow	Outflow
TOTAL PHOSPHORUS								
1976-77	1682	3826	5508	2200	1682	333	2015	99
1977-78	2107	4229	6336	1733	2107	490	2597	101
1978-79	1918	4622	6540	1685	1918	327	2245	219
$\bar{x}$	1902	4226	6128	1873	1902	383	2285	140
DISSOLVED INORGANIC								
1976-77	1314	1019	2333	317	1314	84	1398	60
1977-78	1591	1443	3034	323	1591	124	1715	13
1978-79	1591	1185	2776	344	1591	26	1617	67
$\bar{x}$	1499	1216	2715	328	1499	78	1577	47
DISSOLVED ORGANIC								
1976-77	180	1162	1342	564	180	79	259	25
1977-78	342	1966	2308	670	342	254	596	51
1978-79	235	1945	2180	732	235	94	329	73
$\bar{x}$	252	1691	1943	655	252	142	395	50
PARTICULATE								
1976-77	239	1804	2043	1374	239	192	431	13
1977-78	285	1113	1398	797	285	140	425	38
1978-79	294	1502	1796	697	294	208	502	96
$\bar{x}$	273	1473	1746	956	273	180	453	49

was related to the water budget of each area; rainfall supplied most of the water and phosphorus to the no-flow marsh, while pumped river water was the most important water and phosphorus source for the flow-thru marsh.

The pumping of river water into the flow-thru marsh resulted in a larger annual supply of phosphorus to this area in comparison to the no-flow marsh. The 6128 g/ha annual influx of total P into the flow-thru marsh was nearly three times the 2285 g/ha annual influx primarily through rainfall into the no-flow marsh (Table 6). Supplies of dissolved inorganic, dissolved organic and particulate P to the flow-thru marsh were 1.7, 4.9 and 3.8 times the respective supplies to the no-flow marsh. Again the phosphorus budget of each marsh area was related to the water budget; the additional water supply through pumping resulted in a larger phosphorus supply to the flow-thru marsh.

The flow-thru marsh removed about twice as much phosphorus from the water as the no-flow marsh each year (Table 6). Annual phosphorus retention by the flow-thru marsh amounted to 4255 g/ha for total P, 2387 g/ha for dissolved inorganic P, 1288 g/ha for dissolved organic P and 790 g/ha for particulate P. By comparison, the no-flow marsh removed 2145, 1530, 345 and 404 g/ha/yr of the above four phosphorus fractions, respectively.

TABLE 6. PHOSPHORUS RETENTION (g/ha/yr) BY BONEY MARSH

	FLOW-THRU MARSH			NO-FLOW MARSH		
	Total Influx	g Retention	% Retention	Total Influx	g Retention	% Retention
Total Phosphorus	6128	4255	69%	2285	2145	94%
Dissolved Inorganic	2715	2387	88%	1577	1530	97%
Dissolved Organic	1943	1288	66%	395	345	87%
Particulate	1746	790	45%	453	404	89%

Even though the flow-thru marsh removed more phosphorus per hectare annually than the no-flow marsh, the no-flow area removed a larger percent of the phosphorus supplied to it. The no-flow marsh retained 94% of its annual phosphorus input, while the flow-thru marsh removed only 69% of the phosphorus supplied to it each year (Table 6). Percent phosphorus retention was larger in the no-flow marsh in the case of each phosphorus fraction; dissolved inorganic P was reduced 97% by the no-flow marsh compared to 88% by the flow-thru marsh, dissolved organic P was reduced by the no-flow marsh 87% compared to 66% by the flow-thru marsh and particulate P was reduced 89% by the no-flow marsh compared to 45% by the flow-thru marsh.

Reductions in phosphorus concentration (mg/l) between the river inflow and marsh outflow by the flow-thru area under-estimated the actual phosphorus uptake in grams by this marsh. While phosphorus concentrations in inflowing water were reduced by 37-64% each year, the net annual uptake of phosphorus in grams ranged from 60-74% of the total input. This suggests that studies which derive phosphorus uptake estimates from reductions in surface water concentrations may be under-estimating actual net uptakes by as much as 38%.

Discussion

Phosphorus concentrations averaging .043 mg/l in the river water inflows to the Boney Marsh were well below inflow concentrations which have been reported in most of the nutrient uptake studies done to date. The only example of marsh phosphorus uptake at comparably low inflow concentrations was the study by Banoub (1975) in which the littoral zone of Bodensee received water containing .046 mg P/l, however the 28% reduction in phosphorus concentration reported in that study was relatively low. During the first three year study period, the Boney Marsh reduced total P concentrations in inflowing river water by more than 50%. This efficiency of the Boney Marsh in reducing phosphorus concentrations is surprising, considering the direct relationship between uptake efficiencies and inflow concentrations which is apparent from previous studies. The Boney Marsh met the criterion of Jones and Lee (1978) that a 50% reduction in phosphorus loads would be necessary to make a discernible change in chlorophyll a concentrations in Lake Okeechobee. Thus, the restoration of wetlands on the Kissimmee River floodplain appears at this time to be one feasible alternative to improve Lake Okeechobee water quality during early successional stages following marsh reflooding.

The mean phosphorus concentration of .174 mg/l in Boney Marsh rainfall exceeded mean concentrations in Florida rainfall of .033 mg P/l for north central Florida lakes (Brezonik et al., 1969), .050 - .090 mg P/l for south Florida agricultural sites (Shannon, 1978) and .064 mg P/l for Okeechobee, FL (South Florida Water Management District, Water Chemistry Division, unpublished). Phosphorus concentrations in Boney Marsh rainfall most closely resembled ortho-PO_4 concentrations of .060 - .400 mg P/l which Brezonik (1973) found in urban rainfall near Gainesville, Florida. Urban development does not exist near the Boney Marsh, and reasons for the unusually high phosphorus concentrations in this rainfall are not known. In any case, the unusually high contribution of phosphorus to the Boney Marsh through rainfall appeared to result in a phosphorus mass balance for the marsh which may not be typical in other regions of Florida. The elevated phosphorus inputs through rainfall would particularly affect the no-flow marsh which depended on rain as its primary phosphorus supply. The nutrient supply as well as retention by the no-flow marsh would be expected to be reduced if rainfall phosphorus concentrations were lower.

The mass balances between phosphorus inputs and outputs in the flow-thru and no-flow marshes were strongly related to the hydrology of the areas. The overland flow of river water across the flow-thru marsh supplied 4226 g P/ha/yr to this area, while water fluctuation in the no-flow marsh provided only 383 g P/ha/yr. Rainfall was the largest source of phosphorus to the no-flow marsh, supplying 1902 g/ha/yr. Rainfall was of secondary importance in supplying phosphorus to the flow-thru marsh. The additional phosphorus supply through the overland flow of river water nearly doubled the annual phosphorus retention by the marsh from 2145 g/ha/yr by the no-flow marsh to 4255 g/ha/yr by the flow-thru marsh. The greater annual phosphorus retention by the flow-thru marsh appeared to be related to the larger phosphorus supply from the pumped inflow of river water. In other words, the larger inflow of river water to the flow-thru marsh provided a larger annual supply of phosphorus per hectare, which increased the annual phosphorus uptake. The larger annual phosphorus retention by the flow-thru marsh resulted simply from exposing more water, i.e. phosphorus, to the marsh each year. The restoration of overland flow across selected marsh areas in the Kissimmee River Valley, in addition to annual water level fluctuation, would appear to be more effective in phosphorus removal than water fluctuation alone.

The increased efficiency in percent phosphorus retention by the no-flow marsh possibly was related to the smaller amounts of phosphorus supplied to it. The limited phosphorus supply without flow may have required the marsh to more efficiently utilize what phosphorus was available. Another factor which may have increased the efficiency of percent phosphorus retention by the no-flow marsh was the greater proportion of dissolved inorganic P in rainfall, which was the primary phosphorus supply for this area. Dissolved inorganic P was the phosphorus fraction most readily retained by the marsh. Thus the high content of filterable inorganic P in rainwater would be conducive to increased percent phosphorus uptake by the no-flow marsh.

There was no seasonal phosphorus release by the Boney Marsh as was reported by Federico et al. (1978) for nearby Chandler Slough. Jones and Lee (1978) anticipated such a release from Kissimmee River marshes based on their findings that northern marshes released phosphorus during winter periods of plant dormancy and during dry periods when the water table was below ground level. The Boney Marsh and Chandler Slough differ hydrolgically in that the Boney Marsh does not go completely dry each year under its present water regulation schedule while portions of Chandler Slough generally do. The soluabilization of particulate organic forms of phosphorus which accompanies drying and aeration of marsh soils (Lee et al, 1975) may account for the phosphorus release from Chandler Slough at the beginning of the wet season. Perhaps the absence of a complete dry-down increases the annual net phosphorus retention by these wetlands.

The Boney Marsh acted as a year-round sink for 69% of the phosphorus supplied to it. This is contrary to the prediction of Jones and Lee (1978) that there would probably be a net phosphorus balance over an annual cycle with essentially all nutrients entering Kissimmee River wetlands from upstream being released to the outlet. The success of the Boney Marsh as a phosphorus sink may be related to two factors. The conclusions of Jones and Lee (1978) were based on experience with northern marshes in which biological activity is drastically reduced during the winter period of below-freezing temperatures and ice cover. Seasonal differences in both temperature and biological activity are much less extreme in subtropical wetlands such as the Boney Marsh, and a year-round nutrient demand would be more likely in this situation. The role of the Boney Marsh as a year-round phosphorus sink also may be related to on-going vegetation succession in the area, including an increasing phosphorus storage in both the living and dead plant material from year to year since the area was reflooded in 1975. Pomeroy (1970) viewed succession as "... a process through which populations accumulate enough nutrients to make possible the rise of succeeding populations. Climax communities perpetuate their stability in part by conserving essential elements." Thus as long as the Boney Marsh vegetation continues to undergo succession since reflooding in 1975, it would be expected to act as a phosphorus sink. As the marsh approaches a climax community for the present conditions of water level and nutrient supply, nutrient accumulation might be expected to decline. A future communication on this study will describe the vegetation succession in the Boney Marsh and examine relationships between this succession and the efficiency of the marsh as a phosphorus sink.

NITROGEN

Previous Work

The few studies which have demonstrated reductions in total N concentrations by wetlands suggest that percent uptake efficiencies may be related to nitrogen concentrations in inflows (Table 7). High nitrogen concentrations of 30 and 33 mg/l in inflowing sewage effluent were reduced 83 and 97% by the Lake Balaton reed zone in Hungary (Toth, 1972) and by the meadow-marsh systems in Brookhaven, N.Y. (Small, 1978). Lower nitrogen concentrations averaging 4.7 mg/l in stream water entering Theresa Marsh in Wisconsin were reduced only 40% (Klopatek, 1975), while inflow concentrations of 1.38 mg N/l in surface water entering Chandler Slough, Florida, were not reduced at all (Federico et al., 1978).

Reductions in concentrations of the nitrogen fractions by wetlands appear to be highly variable (Table 7). Changes in the organic N concentration of water passing through wetlands ranged from an 80% uptake by a central Florida swamp/marsh (Boyt et al., 1977) to a 20% release by Theresa Marsh in Wisconsin (Klopatek, 1975). Uptake of organic N has been reported in two wetlands where inflow concentrations were 7.5 - 7.6 mg/l; either no change or an increase in organic N concentrations occurred in two other wetlands where inflow concentrations averaged 1.19 - 1.32 mg/l. Reductions in NO_3 concentrations by wetlands have been found only in Wisconsin and Michigan marshes (Bentley, 1969; Kadlec and Tilton, 1978; Klopatek, 1975). The Santee Swamp in South Carolina did not alter the NO_3 concentration of the river water flowing through it (Kitchens et al., 1975), while Chandler Slough in Florida and the Bodensee reed zone in Germany-Switzerland increased NO_3 concentrations between inflows and outflows (Federico et al., 1978; Banoub, 1975). Reductions in NH_4 concentrations by wetlands vary from almost no change in the Santee Swamp (Kitchens et al., 1975) to nearly complete uptake in a central Florida swamp/marsh (Boyt et al., 1977).

The flux of nitrogen in freshwater marshes is inadequately understood and not subject to many generalizations at this time. Nitrogen cycling in marshes is complicated by the possible loss of nitrogen to the atmosphere through ammonification and denitrification, by the often-overlooked importance of rainfall as a nitrogen source and by the possibility of biological nitrogen fixation occurring within a marsh. Evidence is accumulating that a wide variety of blue-green algae and micro-organisms carry on N fixation as summarized by Painter (1970) and Stewart (1970).

Ammonification (organic $N \rightarrow NH_4$) and denitrification ($NO_3 \rightarrow NH_4$) offer probable explanations for a portion of the nitrogen uptake found in wetlands. Bentley (1969) suggested ammonification to explain the decrease in soluble organic N in Horicon Marsh; however, he pointed out that NH_4-N concentrations did not increase in the marsh water, concluding that immediate uptake of the end product must have occurred. Kadlec and Tilton (1978) attributed the high NH_4-N concentrations in the water of Houghton Lake, Michigan, wetland to ammonification of organic N. Denitrification reactions appeared to occur throughout the year in Theresa Marsh in Wisconsin (Klopatek, 1975). Biological and non-biological denitrification of NO_3 by marsh soils, primarily biological at pH >6.0 and non-biological at pH <6.0, was experimentally demonstrated by Bartlett et al. (1979). These authors found that biological denitrification reduced at least 90% of the added NO_3 to gaseous N_2O and N_2 and that there was little or no transfer of NO_3 to NH_4 or organic N fractions. Thus N_2 loss to the atmosphere rather than storage within the marsh may account for a large part of the decreases in nitrogen concentrations by marshes.

TABLE 7. MEAN NITROGEN CONCENTRATIONS (mg/l) IN SURFACE WATER INFLOWS AND OUTFLOWS OF WETLANDS

Location	Inflow	Outflow	% Change	Source
		TOTAL N		
Lake Balaton, Hungary	32.68	0.86	-97%	Toth, 1972
Meadow/marsh, Brookhaven, NY	30.00	5.00	-83%	Small, 1978
Theresa Marsh, Wisc.[2]	4.72	2.84	-40%	Klopatek, 1975
Chandler Slough, Fla.	~1.38	~1.38	0%	Federico et al, 1978
		ORGANIC NITROGEN		
Cent. Fla. swamp/marsh	7.50	1.50	-80%	Boyt et al, 1977
Horicon Marsh, Wisc. (summer)[3]	7.60	6.30	-17%	Bentley, 1969
Chandler Slough, Fla	~1.32	~1.32	0%	Federico et al, 1978
Theresa Marsh, Wisc.[2]	1.19	1.43	+20%	Klopatek, 1975
		NITRATE		
Horicon Marsh, Wisc. (summer)	1.50	0.10	-93%	Bentley, 1969
Houghton Lake, Mich.	0.36	≳0.06	-83%	Kadlec and Tilton, 1978
Theresa Marsh, Wisc.	1.00	0.89	-11%	Klopatek, 1975
Santee Swamp, S.C.	~0.21	~0.21	0%	Kitchens et al, 1975
Chandler Slough, Fla.[1]	0.028	0.036	+28%	Federico et al, 1978
Bodensee, Germany-Switzerland	0.13	0.27	+107%	Banoub, 1975
		AMMONIA		
Cent. Fla. Swamp/marsh	50.20	~0.00	-100%	Boyt et al, 1977
Theresa Marsh, Wisc.	1.72	0.86	-50%	Klopatek, 1975
Chandler Slough, Fla.	0.05	0.033	-34%	Federico et al, 1978
Bodensee, Germany-Switzerland	0.17	0.12	-29%	Banoub, 1975
Santee Swamp, S.C.	~0.25	~0.25	~0%	Kitchens et al, 1975

[1] Values are for NO_x rather than NO_3 alone

[2] N values for Theresa Marsh represent modal values for the ranges of concentrations in inflows and outflows

[3] Values represent soluable organic N

A source of nitrogen to wetlands which has received inadequate attention in nutrient uptake studies is rainfall. Likens (1975) estimated the average quantity of nitrogen in rainfall from various sources to be 0.80 $g/m^2/yr$. A similar supply of 0.69 g $N/m^2/yr$ was reported by Gore (1968) over a six year period near Moor House, England. A mean annual NO_3 concentration of 0.62 mg/l in rainfall over eastern North Carolina and southeastern Virginia supplied 0.60 g $N/m^2/yr$ to that area (Gambell and Fisher, 1966). Studies of Florida rainfall suggest that it is an important source of nitrogen and that concentrations vary with land use of nearby areas. Rainfall concentrations of .208 mg/l NH_3-N, .209 mg/l NO_3-N and 0.32 mg/l organic N contributed between 15 and 40% of the annual nitrogen supply to north central Florida lakes (Brezonik et al, 1969; Brezonik and Shannon, 1971). Comparison of urban vs rural rainfall in Florida during the summer of 1968 yielded NH_3-N levels of 0.08 - 1.26 mg/l at Gainesville in contrast to 0.03 - 0.08 mg/l at Cedar Key; NO_3-N levels of 0.25 - 1.11 mg/l in rainfall at Gainesville contrasted with .007 - .036 mg/l at Cedar Key (Brezonik, 1973). This data suggested that rainfall nitrogen was elevated by urban land use. Precipitation at south Florida agricultural sites contained 0.57 - 1.01 mg/l total N and 0.47 - 0.66 mg/l dissolved inorganic N (Shannon, 1978), indicating that rainfall nitrogen concentrations at agricultural sites may be intermediate between those at rural, non-agricultural areas and those at urban areas. Nitrogen occurred in significant amounts in rain from each of these areas, and precipitation undoubtedly constitutes an important source of N to marshes.

Results

Nitrogen Concentrations in Water

Significant differences were not found between inflow and outflow concentrations of total N, dissolved organic N or particulate N (Table 3). Total N concentrations in river inflows to the flow-thru marsh generally resembled those in the outflows (Fig. 4). Only the occasional peaks in inflow total N appeared to be reduced by the marsh. There was no discernible seasonal pattern to those peaks, which resulted largely from elevated particulate N. Other than during these peaks, particulate N concentrations were usually close to detection limits of 0.20 mg/l. Inflow and outflow concentrations of dissolved organic N were similar throughout the study, and no pattern was apparent in their fluctuations.

Dissolved inorganic N was the only fraction which was consistently higher in inflows than in outflows of the flow-thru marsh (Fig. 4). Dissolved inorganic N concentrations in inflowing river water increased during fall to early winter each year and were reduced most by the marsh during these periods. Reductions in dissolved inorganic N concentrations between the river inflows and the marsh outflows of the flow-thru area were significant ($p=0.05$) during each year of the study (Table 3). Inflow dissolved inorganic N concentrations of 0.12, 0.09 and 0.08 mg/l averaged annually were reduced 42, 67 and 62% by this marsh during the first, second and third years of the study.

The monthly profiles indicated that most of the decrease in the dissolved inorganic N concentration of river water entering the flow-thru marsh occurred in the upper 0.32 km of the marsh (Fig. 5) in an area encompassing about 9.7 ha. All of the decrease in NO_3 and NO_2 occurred in this upstream reach, and these fractions remained near

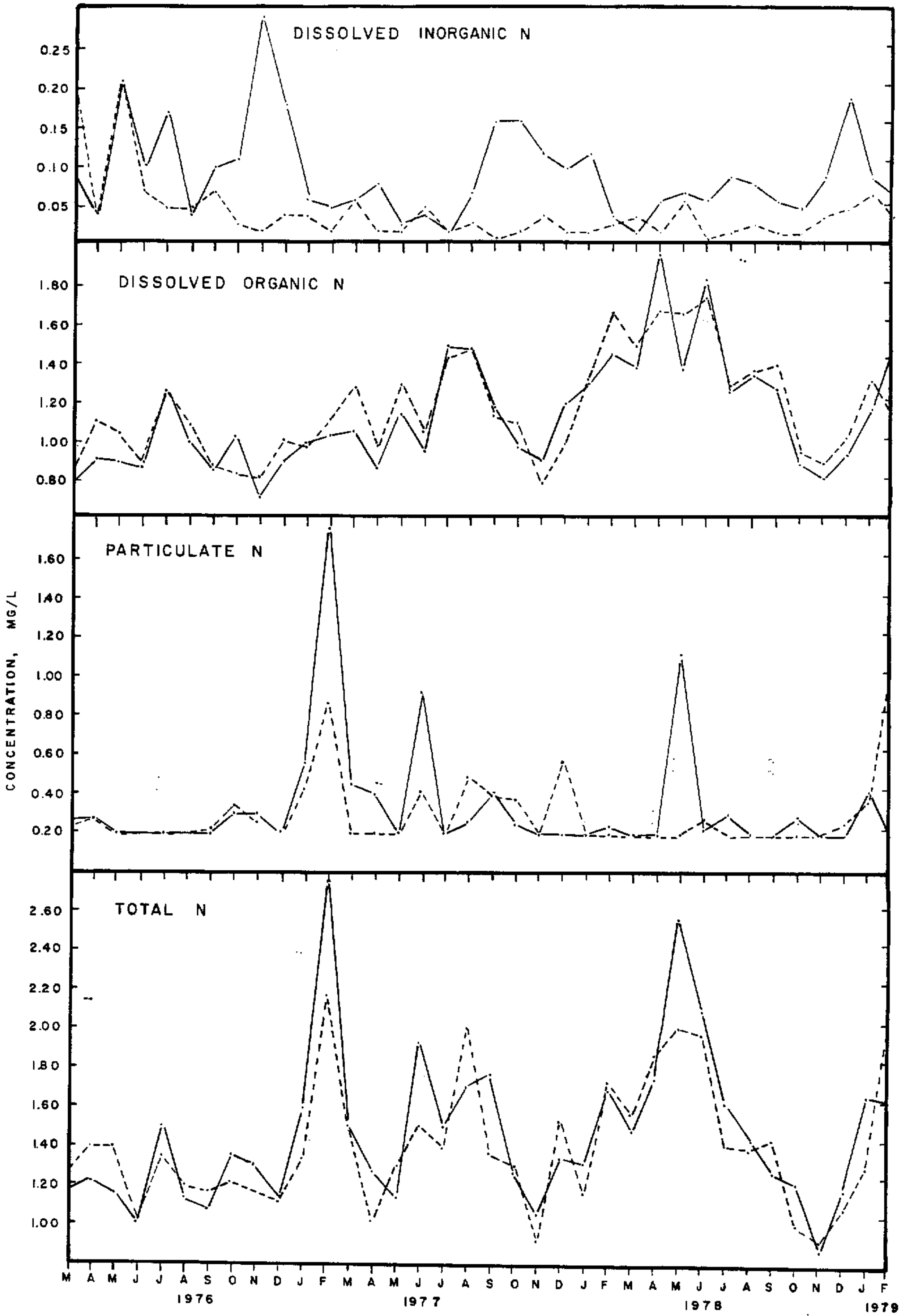

FIG. 4 Monthly average nitrogen concentrations in inflow (solid line) and outflow (dashed line) water of flow-thru marsh.

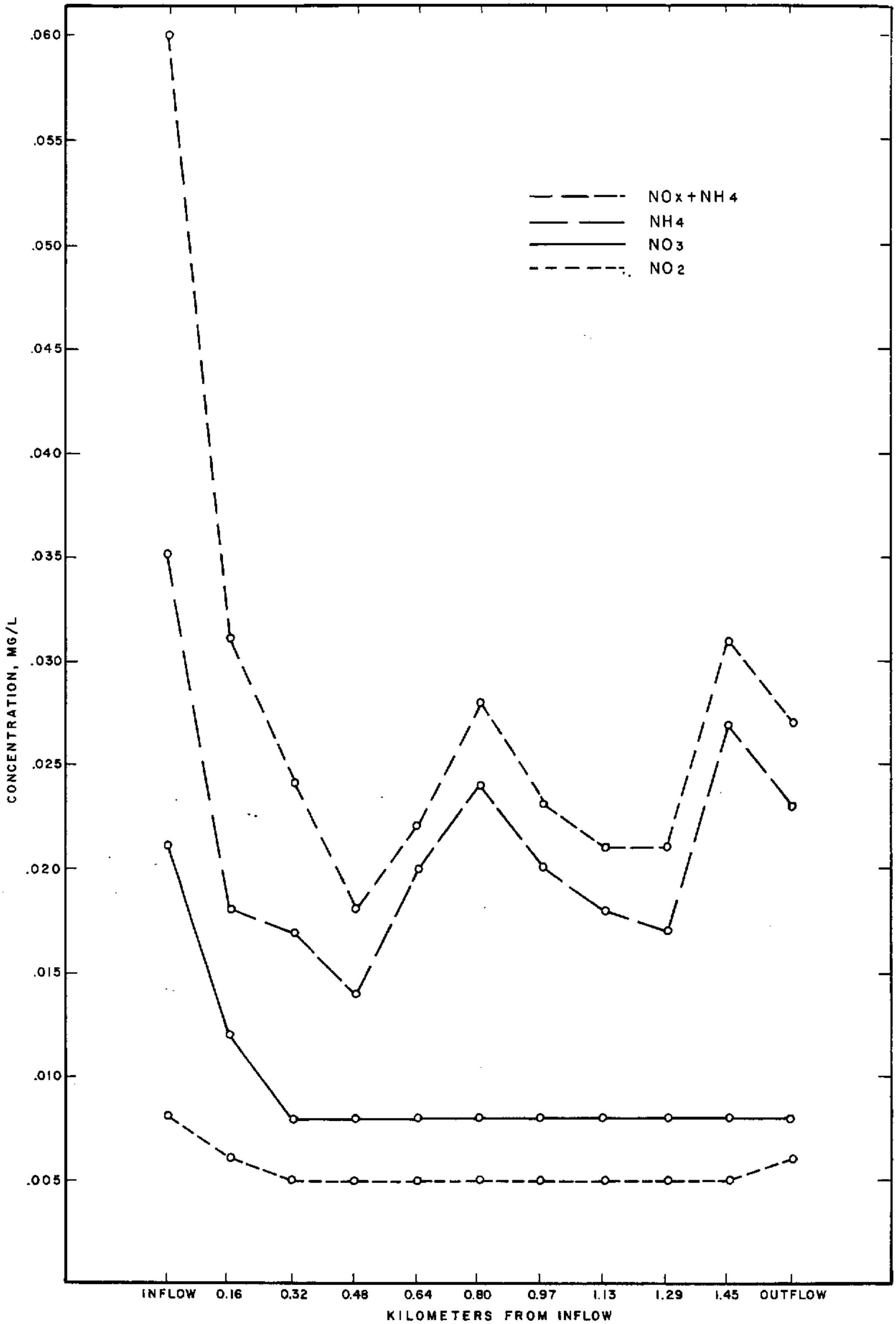

FIG. 5 Reductions in inorganic nitrogen concentrations in the water along the length of the flow-thru marsh.

their detection limits of .008 mg/l for NO_3 and .004 mg/l for NO_2 throughout the remainder of the marsh. Ammonia decreased from .035 to .014 mg/l in the upper 0.48 km of the flow-thru marsh; however, increases to .024 and .027 mg/l occurred in the middle and downstream reaches.

Ammonia and NO_3 concentrations in the river inflows on the dates of the profiles exhibited seasonal patterns which were not evident for dissolved inorganic N as a whole. Ammonia inflow concentrations were highest in summer-fall, averaging .057 mg/l June through November compared to .020 mg/l during the remainder of the year. Nitrate inflow concentrations were $\leq$.008 mg/l except during December, January and February when they averaged .067 mg/l. Nitrite inflow concentrations fluctuated from $\leq$.004 to .019 mg/l with no apparent seasonal pattern.

Rainwater contained higher nitrogen concentrations than the river water inflows. The 2.34 mg/l mean concentration of total N in rain was about 1.6 times the concentration of 1.45 mg/l in river water (Table 4). The largest difference between rain and river water nitrogen was the nearly tenfold increase in dissolved inorganic N in rain water compared to river water. Particulate N concentrations in rain water were 1.4 times the concentrations in river water. Dissolved organic N was the only fraction which had higher concentrations in river water than in rain. The dissolved organic fraction was the largest nitrogen component in both river water and rainfall, making up 81% of the river water nitrogen and 48% of the rainfall nitrogen.

Nitrogen concentrations in the outflow water from the no-flow marsh exceeded those in the outflow from the flow-thru marsh (Table 4). Most of this difference can be attributed to dissolved inorganic N; the mean concentration in the outflow water from the no-flow marsh was nearly twice that in the outflow from the flow-thru marsh. This difference may be related to the major source of water to each of these areas - rainfall for the no-flow marsh and river water for the flow-thru marsh. The higher dissolved inorganic N concentrations in rain compared to river water corresponded to the higher concentrations in outflows of the no-flow marsh compared to the flow-thru marsh.

Nitrogen Budgets

Rainfall supplied most of the nitrogen to the no-flow marsh, while the additional river water inflow to the flow-thru marsh was the major contributor to that area (Table 8). Rain supplied 66% of the total N, 90% of the dissolved inorganic N, 57% of the dissolved organic N and 58% of the particulate N influx to the no-flow marsh. Rainfall was less important in the nitrogen budget of the flow-thru marsh, where 88% of the total N, 90% of the dissolved organic N and 87% of the particulate N were provided through the pumped inflow of river water. The supplies of these nitrogen fractions to each marsh area were controlled by the water budgets. The primary source of water, as well as nitrogen, was rain for the no-flow marsh and river water for the flow-thru marsh. This was not the case for dissolved inorganic N. The high concentrations of dissolved inorganic N in the rainwater supplied 52% of this fraction to the flow-thru marsh in spite of the larger nitrogen influx through pumped river water.

The additional nitrogen entering the flow-thru marsh in the pumped river water resulted in a larger annual supply to this area compared to the no-flow marsh. The 167.9 kg/ha annual influx of total N into the flow-thru marsh was over 4 times the 38.6 kg/ha influx into the no-flow marsh (Table 9). Supplies of dissolved inorganic, dissolved organic and particulate N to the flow-thru marsh were 1.8, 5.8, and 4.5 times the respective supplies to the no-flow marsh. Again the nitrogen budget of each marsh was dependent upon the respective water budget; the additional water supply through pumping resulted in a larger nitrogen supply to the flow-thru marsh.

The annual nitrogen retention of 39.9 kg/ha by the flow-thru marsh exceeded the 31.3 kg/ha retention of the no-flow marsh by about 27% (Table 9). Uptakes of dissolved inorganic, dissolved organic and particulate N by the flow-thru marsh of 14.7, 18.9, and 6.9 kg/ha/yr exceeded the respective uptakes of 10.2, 16.1, and 5.2 kg/ha/yr of the no-flow marsh. The larger annual nitrogen retention by the flow-thru marsh appeared to result from exposing more water, i.e. nitrogen, per hectare to the marsh each year.

Even though the flow-thru marsh removed more nitrogen per hectare than the no-flow marsh, the latter area removed a larger percent of the nitrogen supplied to it annually. The no-flow marsh retained 81% of its annual nitrogen input, while the flow-thru marsh removed only 24% (Table 9). Percent nitrogen retention by the no-flow marsh was larger in the case of each nitrogen fraction: dissolved inorganic N was reduced 97% by the no-flow marsh compared to 80% by the flow-thru marsh, dissolved organic N was reduced 74% by the no-flow marsh compared to 15% by the flow-thru marsh, and particulate N was reduced 77% by the no-flow marsh compared to 23% by the flow-thru marsh. The increased efficiency in percent nitrogen retention by the no-flow marsh may have been related to the smaller amounts of nitrogen supplied to it, the limited supply requiring more efficient utilization by the marsh biota. This increased efficiency may also be related to the high concentrations of dissolved inorganic N in

TABLE 8. ANNUAL INFLUX AND OUTFLUX (kg/ha/yr) OF NITROGEN IN THE BONEY MARSH

	FLOW-THRU MARSH				NO-FLOW MARSH			
	Rain	River Inflow	Total Inflow	Outflow	Rain	River Inflow	Total Inflow	Outflow
TOTAL NITROGEN								
1976-77	23.7	137.0	160.7	113.6	23.7	12.4	36.1	5.6
1977-78	21.2	143.9	165.1	127.2	21.2	15.5	36.7	5.6
1978-79	32.0	146.1	178.0	143.4	32.0	11.2	43.2	10.8
$\bar{x}$	25.6	142.3	167.9	128.1	25.6	13.0	38.6	7.3
DISSOLVED INORGANIC								
1976-77	9.8	10.9	20.7	<5.1	9.8	1.4	11.2	0.5
1977-78	9.1	8.7	17.8	<2.4	9.1	1.2	10.3	0.1
1978-79	9.7	7.3	17.1	<3.7	9.7	0.4	10.2	0.4
$\bar{x}$	9.5	9.0	18.5	<3.7	9.5	1.0	10.6	0.3
DISSOLVED ORGANIC								
1976-77	10.8	96.5	107.4	92.2	10.8	7.8	18.6	2.8
1977-78	9.3	117.1	126.4	104.8	9.3	11.8	21.1	5.0
1978-79	17.2	130.9	148.1	128.2	17.2	8.6	25.8	9.3
$\bar{x}$	12.4	114.8	127.3	108.4	12.4	9.4	21.8	5.7
PARTICULATE								
1976-77	3.1	34.7	37.9	20.3	3.1	3.2	6.4	2.3
1977-78	3.2	26.4	29.5	26.4	3.2	2.6	5.8	0.7
1978-78	5.4	17.9	23.3	23.2	5.4	2.5	7.9	1.6
$\bar{x}$	3.9	26.3	30.2	23.3	3.9	2.8	6.7	1.5

TABLE 9. NITROGEN RETENTION (kg/ha/yr) BY BONEY MARSH

	FLOW-THRU MARSH			NO-FLOW MARSH		
	Total Influx	g Retention	% Retention	Total Influx	g Retention	% Retention
Total Nitrogen	167.9	39.9	24%	38.6	31.3	81%
Dissolved Inorganic	18.5	14.8	80%	10.6	10.2	97%
Dissolved Organic	127.3	18.9	15%	21.8	16.1	74%
Particulate	30.3	6.9	23%	6.7	5.2	77%

rainfall, which was the primary nitrogen source of the no-flow marsh. Dissolved inorganic N probably was more readily available than the other nitrogen fractions for biological uptake, and this may have resulted in a more complete extraction of nitrogen by the no-flow marsh.

The 39.9 kg/ha nitrogen retention by the flow-thru marsh, which amounted to an uptake of 24% of the nitrogen input, became evident only when the nitrogen budget for the area was considered. The nitrogen concentrations alone in the inflowing and outflowing water did not reveal any net annual uptake because they did not account for the supply of nitrogen by rainfall or the concentration of nitrogen in outflows due to evapotranspiration.

Discussion

The lack of change in total N and organic N concentrations between inflow and outflow is consistent with the results of Federico et al (1978) for Chandler Slough. Reductions in dissolved inorganic N concentrations from .097 to .043 mg/l by the flow-thru marsh in this study were larger than reductions from .078 to .069 mg/l by Chandler Slough (Federico et al., 1978). Most of the difference in dissolved N uptake by the two wetlands was due to the highly efficient NO_3 uptake in the upper reach of the flow-thru marsh, as indicated by the profiles, compared to the net annual release of NO_3 by Chandler Slough (Federico et al., 1978). The reduction in NH_4 concentration of .035 to .023 mg/l by Boney Marsh, based on the profiles, was slightly less than the .050 to .033 mg/l reduction reported for Chandler Slough (Federico et al., 1978). Ammonia increases in the lower reaches of the Boney Marsh flow-thru area may well have resulted from denitrification of NO_3 and/or ammonification of organic matter within the marsh, as has been suggested for other wetlands by Bentley (1969), Kadlec and Tilton (1978) and Klopatek (1975). The seasonal increases of NH_4 during summer and NO_3 during winter in inflowing river water suggest that denitrification and/or ammonification rates in the river increase during summer and decrease during winter.

The nitrogen content of Boney Marsh rainfall was well above that previously reported for other areas. Rainfall's contribution of about 2.5 g/m^2/yr to the nitrogen mass balance of the Boney Marsh was over three times the global average reported by Likens (1975). The mean total N concentration in Boney Marsh rainfall of 2.34 mg/l was about two to four times the mean concentrations of 0.57 - 1.01 mg/l which Shannon (1978) reported for south Florida agricultural sites. The 0.87 mg/l concentration of dissolved inorganic N in Boney Marsh rainfall was 1.3 - 1.8 times Shannon's values. Rainfall at Okeechobee, FL, contained average concentrations of only 1.08 mg/l total N and 0.61 mg/l dissolved inorganic N (South Florida Water Management District, Water Chemistry Division, unpublished). The atypically high nitrogen concentrations in Boney Marsh rainfall cannot be explained at this time. The mass balances indicated the importance of rainfall as a source of nitrogen to this marsh; rainfall contributed 66% of the total N input to the no-flow area and 12% to the flow-thru area.

The nitrogen mass balance indicated that the marsh was accumulating nitrogen each year even though inflow and outflow concentrations of total N were similar. The flow-thru marsh accumulated nearly 40 kg N/ha/yr which amounted to 24% of its annual nitrogen supply, while the no-flow marsh accumulated about 31 kg N/ha/yr which amounted to 81% of its annual supply. Nitrogen mass balances are virtually lacking in previous nutrient uptake studies, and this may account in part for the highly variable results of these studies.

CATIONS AND CHLORIDE

Previous Work

In studies where cation concentrations have been reported to change between wetland inflows and outflows, the changes involved seasonal uptake and release and occurred in temperate latitudes. Bentley (1969) found calcium and magnesium to decrease during spring and to increase during winter within Horicon Marsh in Wisconsin. Bentley noted that lower concentrations of these elements in discharge water occurred under oxidizing conditions in the marsh, while higher concentrations occurred under reducing conditions accompanying ice cover. Klopatek (1975) reported seasonal changes in Theresa Marsh, Michigan, where decreased potassium concentrations in outflows coincided with peak macrophyte production, and increased outflow concentrations coincided with macrophyte leaching and with increases in available K within the soil. Calcium concentrations in Theresa Marsh outflows fluctuated more erratically and appeared to be related to carbonate precipitation from algal blooms, changes in exchangeable Ca within the soil, ash accumulation by macrophytes and the leaching of ions from macrophytes (Klopatek, 1975). Dilution by groundwater and loss to subsurface water may reduce wetland outflow concentrations of cations and chloride, as has been suggested by Bentley (1969) and Kadlec and Tilton (1978). Other studies have reported no reductions in cation and Cl concentrations by wetlands. Banoub (1975) found that concentrations of Ca, Mg, and Cl remained about the same in water passing through the reed zone and into open water of Bodensee in Germany-Switzerland. Federico et al. (1978) reported no significant reductions in Na, Ca, K, Mg, or Cl concentrations between the inflows and outflows of Chandler Slough, Florida.

The supply of cations and Cl through rainfall has not received much attention in wetland uptake studies. Gorham (1961) reviewed concentrations of these elements in rainfall at various latitudes in the northern hemisphere and reported ranges of 0.6 to 1.2 mg/l for Ca, <0.1 to 0.3 mg/l for Mg, 0.2 to 5.2 mg/l for Na, 0.2 to 0.3 mg/l for K and 0.1 to 8.9 mg/l for Cl (Moore and Bellamy, 1974). Larger variations in rainfall Na and Cl resulted from high values near coastal areas. This has been demonstrated in Florida by Brezonik (1973) who reported decreases in rainfall cation concentrations between Cedar Key and 20 miles inland: modal concentrations dropped from 0.98 to 0.26 mg/l for Ca, from 1.64 to 0.04 mg/l for Mg, from 6.50 to 0.36 mg/l for Na and from 1.00 to 0.13 mg/l for K. Modal rainfall concentrations of Na, K and Cl of 1.10, 0.22 and 2.04 mg/l respectively at south Florida agricultural sites (Shannon, 1978) were slightly higher than Brezonik's values inland of Cedar Key, suggesting that agricultural activity may locally increase rainfall cation concentrations.

Results

Cation and Chloride Concentrations in Water

Potassium was the only cation which decreased in concentration between the inflow and outflow of the flow-thru marsh each year (Table 3). Average K concentrations dropped 30% between inflow and outflow from 0.90 to 0.63 mg/l during the first year, 20% from 1.30 to 1.04 mg/l during the second year and 12% from 0.97 to 0.85 mg/l during the third year. Outflow concentrations of K were generally below inflow concentrations during the first two years of the study (Figure 6), however there was no consistent decrease between inflow and outflow concentrations during the third year. Differences between inflow and outflow K concentrations were significant (p=0.05)

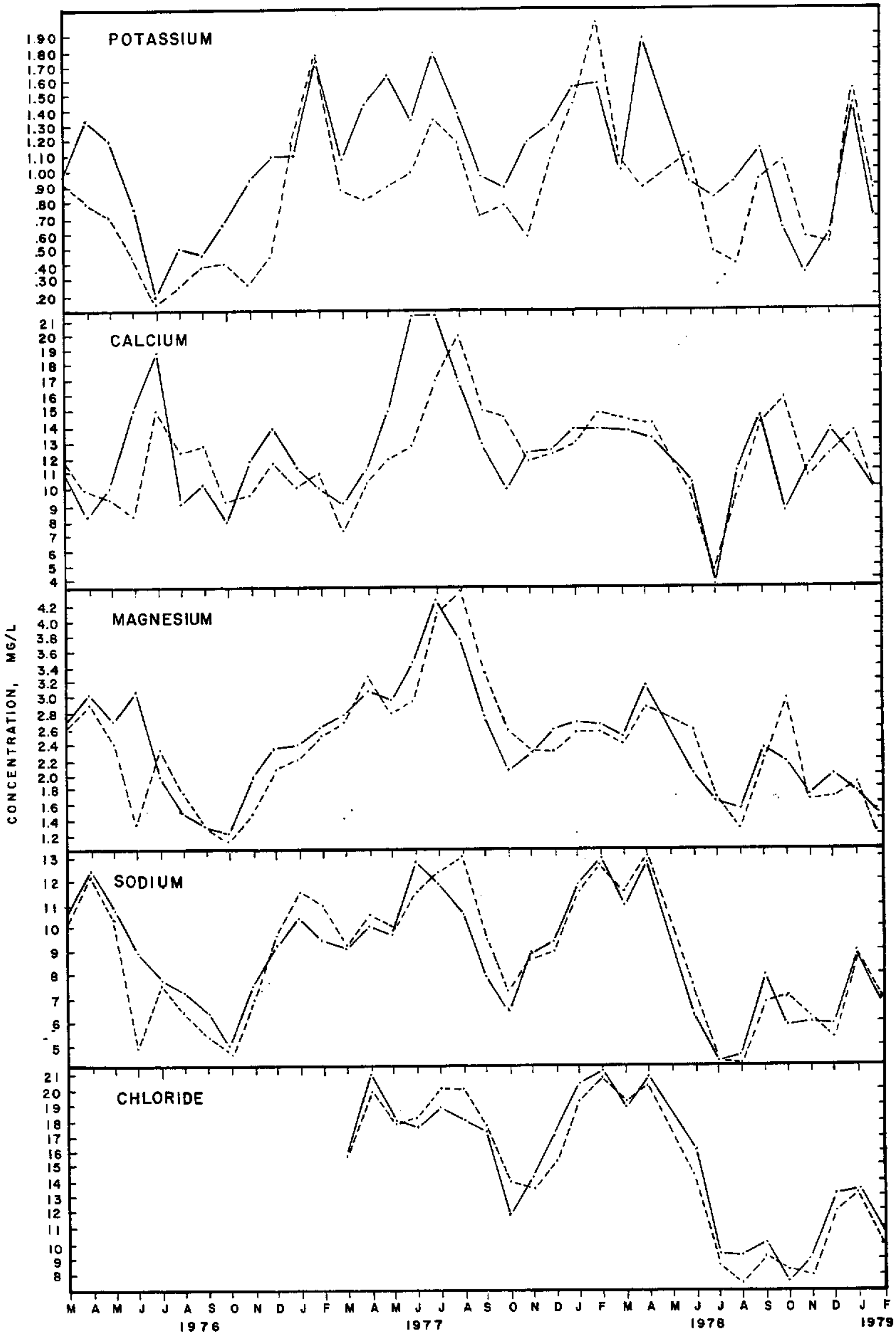

FIG. 6 Monthly average cation and chloride concentrations in inflow (solid line) and outflow (dashed line) water of the flow-thru marsh.

of the supply to the no-flow marsh. Supplies of cations and Cl in river water entering the flow-thru marsh exceeded the supplies to the no-flow marsh about tenfold (Table 11). In spite of the increased supplies to the flow-thru marsh, the two areas retained similar amounts of Mg, Ca, and Cl annually. In contrast to these elements, increased supplies of K and Na to the flow-thru marsh resulted in increased annual retention from 12.0 to 31.9 kg/ha for K and from 23.9 to 41.1 kg/ha for Na.

Uptakes of Mg, Ca, Na, and Cl expressed as percent of the total influx were negligible in the flow-thru marsh and increased to 34-48% in the no-flow marsh; the percent uptake of K increased from 29% in the flow-thru marsh to 76% in the no-flow marsh (Table 11).

TABLE 11. RETENTION OF CATIONS AND CHLORIDE (kg/ha/yr) BY BONEY MARSH

	FLOW-THRU MARSH			NO-FLOW MARSH		
	Total Influx	Kg Retention	% Retention	Total Influx	Kg Retention	% Retention
Potassium	111.3	31.9	29%	15.8	12.0	76%
Magnesium	229.2	13.0	6%	21.4	10.3	48%
Calcium	1175.7	40.3	3%	97.0	42.3	44%
Sodium	856.5	41.1	5%	70.0	23.9	34%
Chloride	1731.7	66.3	4%	145.4	65.9	45%

during the first two years of the study but not during the last. Thus the marsh appeared to become progressively less efficient from year to year in retaining K.

Outflow concentrations of Ca, Mg, Na, and Cl generally followed inflow concentrations (Figure 6). Concentrations of each of these elements generally fluctuated together; however, consistent seasonal patterns were not evident in their fluctuations. Reductions in Ca, Mg, Na, and Cl between inflows and outflows often occurred during periods of rising concentrations; increases between inflows and outflows often occurred during periods of declining concentrations. Averaged over each year of the study (Table 3), concentrations of these elements were not found to be significantly different between inflows and outflows with the following exceptions. A 10% decrease in Mg from 2.21 to 1.99 mg/l was found significant (p=0.05) during the first year of the study, and a five percent decrease in Cl from 12.8 to 12.1 mg/l was found significant (p=0.05) during the last year.

Cation and Cl concentrations in rainfall usually fell below detection limits with the exception of K (Table 4). The average K concentration of 0.54 mg/l in rain was about half the level in river water inflows. Outflow concentrations of K from the no-flow marsh resembled those from the flow-thru marsh, even though one area received mostly rain water and the other mostly river water.

Cation and Chloride Budgets

Cations and Cl were supplied to each marsh area primarily through river water inflows (Table 10). Inputs of Mg, Ca, Na, and Cl in rain were not detectable, while rainfall inputs of K averaging 5.9 kg/ha/yr amounted to only five percent of the total supply to the flow-thru marsh and 37%

TABLE 10. ANNUAL INFLUX AND OUTFLUX (kg/ha/yr) OF CATIONS AND CHLORIDE IN THE BONEY MARSH

	FLOW-THRU MARSH				NO-FLOW MARSH			
	Rain	River Inflow	Total Inflow	Outflow	Rain	River Inflow	Total Inflow	Outflow
POTASSIUM								
1976-77	4.8	87.2	92.1	53.0	4.8	9.2	14.1	1.0
1977-78	5.1	132.7	137.8	92.0	5.1	12.7	17.8	4.3
1978-79	7.9	96.3	104.2	93.2	7.9	7.7	15.6	6.1
$\bar{x}$	5.9	105.4	111.3	79.4	5.9	9.9	15.8	3.8
MAGNESIUM								
1976-77	-(1)	205.8	-(2)	178.2	-(1)	16.9	-(2)	6.6
1977-78	-	283.0	-	257.7	-	32.6	-	12.0
1978-79	-	198.7	-	212.5	-	14.6	-	14.8
$\bar{x}$	-	229.2	-	216.1	-	21.4	-	11.1
CALCIUM								
1976-77	-	1115.5	-	1000.6	-	69.6	-	41.4
1977-78	-	1304.2	-	1172.9	-	157.2	-	56.5
1978-79	-	1107.3	-	1232.5	-	64.3	-	66.2
$\bar{x}$	-	1175.7	-	1135.3	-	97.0	-	54.7
SODIUM								
1976-77	-	847.4	-	742.8	-	62.0	-	29.1
1977-78	-	984.6	-	920.4	-	100.0	-	46.3
1978-79	-	737.6	-	783.2	-	48.1	-	62.9
$\bar{x}$	-	856.5	-	815.4	-	70.0	-	46.1
CHLORIDE								
1976-77	-	-	-	-	-	-	-	
1977-78	-	2203.2	-	2088.2	-	195.6	-	72.0
1978-79	-	1260.2	-	1242.7	-	95.2	-	87.0
$\bar{x}$	-	1731.7	-	1665.4	-	145.4	-	79.5

(1) Concentrations of Mg, Ca, Na and Cl in rain were below detection limits

(2) River inputs of Mg, Ca, Na and Cl are taken as total inputs

Discussion

The reductions in concentration of Na, Ca, Mg, and Cl between inflow and outflow during periods of rising inflow concentrations, and the increases between inflow and outflow during periods of declining concentrations, suggest that an active cation balance may have been operating in the flow-thur marsh. The marsh appeared to assimilate cations during periods of high concentrations in inflow waters and to leech cations during low concentrations in inflow waters. The non-significant differences in concentrations of Na, Ca, Mg, and Cl between the inflows and outflows of the Boney Marsh are consistent with the findings of Federico et al. (1978) for Chandler Slough. The 12-30% annual reductions in K concentrations by the Boney Marsh also compare favorably with 0-36% reductions by Chandler Slough (Federico et al., 1978).

Cation and Cl concentrations in Boney Marsh rainfall resembled rainfall concentrations at Okeechobee, FL (South Florida Water Management District, Water Chemistry Division, unpublished). Rainfall concentrations of Na, Ca, Mg, and Cl were near to or below detection limits at both locations. Mean K concentrations of 0.46 mg/l at the Boney Marsh and 0.54 mg/l at Okeechobee were similar. Concentrations of the cations and Cl in rainfall were well below those found in surface water both in the Boney Marsh and in Chandler Slough. Thus, rainfall would appear to dilute surface water concentrations of these elements rather than increase them.

Annual retentions of Mg, Ca, and Cl by the no-flow marsh appeared to represent the maximum capacity of the marsh to accumulate these elements. When supplies of Mg, Ca, and Cl were increased more than tenfold in the flow-thru marsh, their annual retentions remained about the same. The marsh reacted differently to increased supplies of K and Na; larger inputs of these elements to the flow-thru side were accompanied by increased annual retentions, suggesting the uptake capacity of the marsh for K and Na may increase as the supply increases.

SUMMARY

This study investigates mineral retention by a Kissimmee River marsh and determines the extent to which overland flow augments this retention. Reductions in mineral concentrations in river water flowing across the marsh are estimated, and mineral budgets considering all inputs and outputs are provided. The study was conducted in the Boney Marsh experimental area on the Kissimmee River floodplain during a 3-yr period following re-flooding. An annually fluctuating water regime resembling average conditions before channelization was maintained in the area. The experimental area was divided into two parts, one subjected to nearly continuous flow of pumped river water (flow-thru) and the other subjected to more stagnant conditions (no-flow) where flow resulted primarily from rainfall and water level fluctuation.

Mean total P concentrations in river water of 0.035-0.047 mg/l were significantly reduced by 37-64% between the inflow and outflow of the flow-thru marsh each year. Significant decreases were also found in dissolved inorganic and dissolved organic phosphorus concentrations. The marsh became progressively more efficient from year to year in reducing inflow phosphorus concentrations. The only nitrogen fraction which was significantly reduced in concentration was dissolved inorganic N; mean inflow concentrations of 0.08-0.12 mg/l were reduced 42-62% annually by the flow-thru marsh. No net reductions in cation or chloride concentrations were apparent except for potassium.

Rainfall comprised an important input of phosphorus and nitrogen to both marsh areas. The mean total P concentration of 0.174 mg/l in rainfall

exceeded that in river water by about fourfold. Rainwater total N averaged 2.34 mg/l, which was about 1.6 times the mean concentration in river water. Most of the phosphorus and nitrogen in rainwater was in a dissolved inorganic form. Annual net phosphorus uptakes by the marsh would have been underestimated by as much as 38% if rainfall and evapotranspiration were not considered in the phosphorus budgets. Nitrogen uptake by the marsh became apparent only after rainfall and evapotranspiration were considered.

Phosphorus and nitrogen budgets to the two marsh areas were strongly influenced by the water budgets. Rainfall contributed about half of the water supply and the majority of the phosphorus and nitrogen inputs to the no-flow marsh each year. The additional river water inflow to the flow-thru marsh contributed most of the annual supply of water as well as phosphorus and nitrogen to that area. The overland flow of river water increased the annual water supply to the marsh from 19,500 to 109,300 m^3/ha, increased the annual phosphorus supply from 2.28 to 6.13 kg/ha and increased the annual nitrogen supply from 38.6 to 167.9 kg/ha. The additional phosphorus and nitrogen supplies from overland flow resulted in larger retention of these elements by the marsh. Overland flow increased annual phosphorus retention from 2.14 to 4.26 kg/ha and increased annual nitrogen retention from 31.3 to 39.9 kg/ha.

Both the flow-thru and no-flow areas of the Boney Marsh acted as year-round sinks for phosphorus and nitrogen. No seasonal release of these elements was found, in contrast to the findings of Federico et al. (1978) that nearby Chandler Slough released nutrients upon reflooding following the spring dry period. Boney Marsh soils remained flooded during this study, which may explain the absence of a seasonal nutrient release.

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APPENDIX A. ANALYTICAL METHODS FOR WATER CHEMISTRY DETERMINATIONS.

AutoAnalyzer II Method

Determination	Method	Range	Sensitivity	Detection Limit
Ammonia	Colorimetric Automated Phenate, Technicon AA II Method #154-71W, modified EPA Method #350.1	0-0.50 mg/l	0.01 mg/l	0.01 mg/l
Chloride	Colorimetric Automated Ferricyanide, Technicon AA II Method #99-70W, modified EPA Method #325.2	0-200.0 mg/l	2.0 mg/l	4.0 mg/l
Nitrite	Colorimetric Automated Diazotization with Sulfanilamide and coupling with N-(1 naphthyl) ethylenediamine dihydrochloride, Technicon colorimetric, automated AA II Method #120-70W, modified EPA Method #353.2	0-0.200 mg/l	0.002 mg/l	0.004 mg/l
Nitrate	Same as nitrite with Cadmium Reduction Column. Technicon AA II Method #100-70W, modified EPA Method #353.2	0-0.200 mg/l	0.002 mg/l	0.004 mg/l
Total Kjeldahl Nitrogen	Colorimetric, Semi-automated Block Digestor, Technicon AA II Method #376-75W, 334-74A, modified EPA Method #351.2	0-10.0 mg/l	0.1 mg/l	0.20 mg/l
Ortho Phosphate	Colorimetric, Automated, Phosphomolybdenum Blue Complex with Ascorbic Acid Reduction, Technicon AA II Method #155-71W, modified EPA Method #365.1	0-0.10 mg/l	0.001 mg/l	0.002 mg/l
Total Phosphate	Colorimetric, Semi-automated Persulfate Digestion followed by same method as Ortho Phosphate Technicon AA II Method #155-71W, modified EPA Method #365.1	0-0.10 mg/l	0.001 mg/l	0.002 mg/l

Metals - Major Cation

Atomic Absorption

Determination	Method	Range	Detection Range
Sodium	Atomic Absorption Direct Aspiration with Dual Capillary System (DCS), EPA Method #273.1	0-150 mg/1	As calculated from absorbance
Potassium	Atomic Absorption Direct Aspiration with Dual Capillary System (DCS), EPA Method #258.1	0-10 mg/1	As calculated from absorbance
Calcium	Atomic Absorption Direct Aspiration with Dual Capillary System (DCS), Samples are treated with La_2O_3/HCl with DCS, EPA Method #215.1	0-150 mg/1	As calculated from absorbance
Magnesium	Atomic Absorption Direct Aspiration with Dual Capillary System (DCS), Same treatment as calcium, EPA Method #242.1	0-40 mg/1	As calculated from absorbance