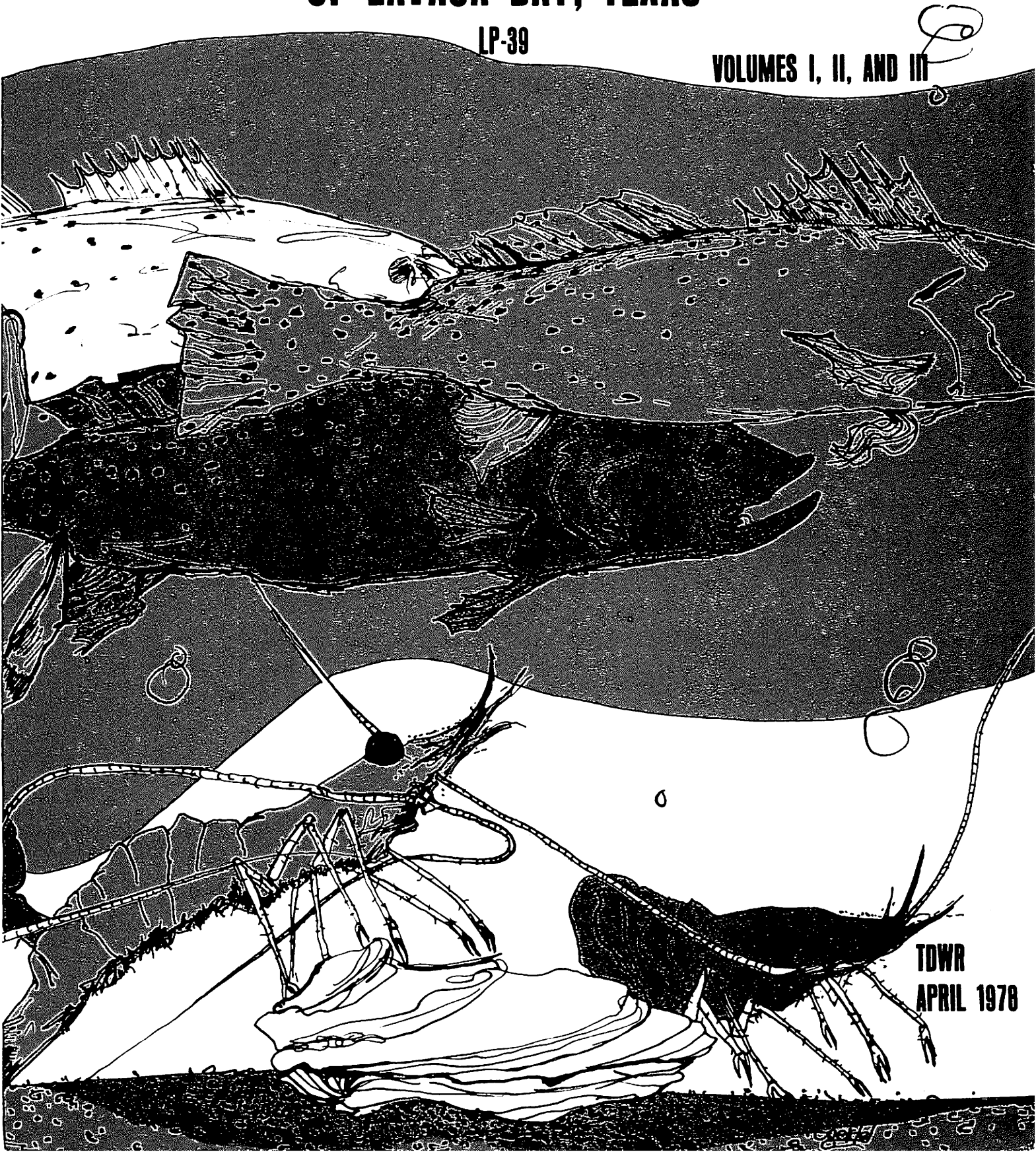# BIOGEOCHEMICAL CYCLING OF CARBON, NITROGEN, AND PHOSPHORUS NUTRIENTS IN RIVER DELTA MARSHES OF LAVACA BAY, TEXAS

LP-39

VOLUMES I, II, AND III

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BIOGEOCHEMICAL CYCLING OF CARBON,
NITROGEN, AND PHOSPHORUS NUTRIENTS IN
RIVER DELTA MARSHES OF LAVACA BAY, TEXAS

BAYS AND ESTUARIES PROGRAM

THREE TECHNICAL REPORTS

Submitted under interagency contracts to
the Texas Water Development Board by the Center for
Research in Water Resources, The University of Texas at Austin

Texas Department of Water Resources

LP-39

February, 1978

PREFACE

The Texas Water Development Board initiated the Bays and Estuaries Program in 1967 to collect biological and hydrological data for the purpose of developing a working knowledge of the relationships that exist among freshwater inflows, tidal exchange, nutrients, and biological productivity of the bays and estuaries. At the time these studies were begun, there were very little reliable data available on the Texas estuarine systems. Although several limited programs were underway, they were largely independent of one another, the data collected under any single program were not comprehensive, and since sampling and measurements of physical parameters under different programs were not accomplished simultaneously, the resulting data could not be reliably correlated.

The Texas Water Code directs the Texas Water Development Board (now the executive body of the Texas Department of Water Resources as a result of consolidation of state water agencies by the 65th Texas Legislature, 1977) to "prepare, develop, and formulate a comprehensive state water plan", wherein, "the Board shall also give consideration in the plan to the effect of upstream development on the bays, estuaries, and arms of the Gulf of Mexico, and to the effect of the plan on navigation" (Chapter 11, Section 11.101, V.T.C.A.). Codified from the Texas Water Development Board Act (1957), these statute provisions were the first legislative directives to focus water resources planning and development on the real problems associated with alteration and/or depletion of riverine freshwater flows.

In 1975, the 64th Texas Legislature amended the Texas Water Code to read:
> "It is the public policy of the State to provide
> for the conservation and development of the State's
> natural resources, including...the maintenance of
> a proper ecological environment of the bays and
> estuaries of Texas and the health of related living
> marine resources" (Chapter 1, Section 1.003, V.T.C.A.).

In so doing, the Legislature further directed that,
> "the [Water Development] Board shall carry out com-
> prehensive studies of the effects of freshwater
> inflows upon the bays and estuaries of Texas,
> which studies shall include the development of
> methods of providing and maintaining the ecolo-
> gical environment thereof suitable to their
> living marine resources" (Chapter 11, Sub-Chapter
> D, Section 11.108, V.T.C.A.).

In response to the legislative mandate, the Board's Bays and Estuaries Program is seeking to establish a broad understanding of the Texas coastal environments and their natural processes. This report, entitled "Biogeochemical Cycling of Carbon, Nitrogen, and Phosphorus Nutrients in River Delta Marshes of Lavaca Bay, Texas", is a consolidation

of three related Bays and Estuaries Program studies performed by the Center for Research in Water Resources, The University of Texas at Austin, under interagency contract with the Board.

The process of nutrient biogeochemical cycling is vital to estuarine productivity and basic to the natural assimilation of nutritive wastes. Moreover, it is intimately tied to fluctuations in freshwater inflows and the inundation and dewatering of the deltaic marsh wetlands. Thus, these reported studies are in direct support of the Board's legislative mandate and make a fundamental contribution to the ecology of Texas bays and estuaries.

CONTENTS

PART I:

BIOGEOCHEMICAL CYCLING OF CARBON, NITROGEN,
AND PHOSPHORUS IN SALTWATER MARSHES
OF LAVACA BAY, TEXAS

by

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CHAPTER I

INTRODUCTION

NEED FOR STUDY

Saltwater marshes and grassflats have been shown to play an extremely important role in providing organic and inorganic food material to a variety of biota in estuaries. Numerous studies along the Atlantic coast of the United States have delineated the pathways of marsh-produced detritus, measured the productivity of the emergent vegetation and associated periphyton of the marsh, and shown the effect of organic waste and associated nutrients on the growth and species composition of the saltwater marsh system.

Saltwater marshes in the Texas coastal zone are presumed to be just as important to the Texas Bays as they are elsewhere; however, little work has been conducted on any of the Texas marshes to measure their productivity, their contributions of organic and inorganic nutrients to the adjacent estuarine waters, or the importance of tidal action and/or freshwater flows to the marsh. The areal distribution of saltwater and freshwater marshes is being mapped in the Texas coastal zone by the Bureau of Economic Geology (e.g. Fisher, et al. 1972). Some work has been done on submerged grassflats in Texas, but only to define their overall distribution, function and importance as habitats for fish and shellfish.

Too, there is a dearth of information on the possible impact of water resouce development on marshes and grassfl..ts. Modifications to freshwater flows and flow periods can effect the function of, nutrient supplies for, and geochemical cycling in these natural systems. These effects are not fully understood at the present time, but they are receiving considerable attention.

The Texas Water Development Board is now developing a hydrodynamic-water quality mathematical model of the Lavaca River-Lavaca Bay-Matagorda Bay system to aid in assessing the impact of water resource development in the Lavaca River and Garcitas Creek basins. The marshes and grassflats of Lavaca Bay are integral parts of the models, but information on the biogeochemical cycles of carbon (organic nutrient) and nitrogen and phosphorus (inorganic nutrients) are needed, especially the exchange rates between the sediments and biota of the marsh and grassflat systems and the water flowing through them.

OBJECTIVES

It was the purpose of this project to perform studies leading to descriptions of the biogeochemical cycles of carbon (C), nitrogen (N), and phosphorus (P) in the saltwater marshes of Lavaca Bay and to state these descriptions in a quantitative form suitable for inclusion in the Board's mathematical model.

SCOPE

Both laboratory and field tests were conducted. Special sediment slurry uptake studies were performed for the purpose of developing Freundlich-like isotherms relating sediment concentrations of C, N. P to the equilibrium concentrations in water and to show the effects of sediment composition, salinity, and temperature on uptake. The flux of N and P into and out of sediment were studied in fixed-bed systems by continuously adding various amounts of N and P to these systems and following uptake in the sediments until equilibrium conditions were established, then stopping the additions and following the release of nutrients from the sediments. Also, portions of the marsh were isolated in several cylindrical plexiglass chambers in the laboratory and nutrient exchange studies performed. Mass balances were made for C, N, and P added in spiked and non-spiked Bay water, and productivity measurements were taken to determine the stimulatory effects of these nutrient additions.

The field studies involved the collection of hydraulic and nutrient data at several stations in a bayou off Swan Lake in Lavaca Bay to determine net nutrient transport and exchange from and in the saltwater marshes. Three field trips were made covering flooded, dry, and moderately wet conditions in the marsh.

From these studies, mathematical models describing the sediment uptake of C, N, and P as a function of the mass transfer coefficient and the difference between equilibrium (as related to the sediments) and ambient nutrient concentrations were to be developed. These models were to be of such form as to be used directly in the Board's larger water quality model.

REPORT ORGANIZATION

The organization of this report is as follows. Chapters are numbered by Roman numerals, and pages, tables, and figures are numbered within

individual chapters using the chapter Roman numeral followed by an Arabic numeral (e.g. II-1, IV-2, etc.). Figures are placed at the end of each chapter.

The results of the literature review are presented in Chapter II followed by the methods used in this study in Chapter III. Results of the field and laboratory investigations are contained in Chapter IV, and the results are discussed in Chapter V. Finally, the conclusions of this study and recommendations for future work are given in Chapter VI.

ACKNOWLEDGMENTS

CHAPTER II

PREVIOUS WORK

NATURE OF LITERATURE REVIEW

The review of previous work in the literature was limited specifically to two areas: nutrient exchange studies with sediments and marsh plants; and laboratory models or microcosms of marsh ecosystems. The two areas of study were chosen since this project focused on the biogeochemical cycling of nutrients in the marsh and hence a determination of the rate of nutrient movement from one marsh component to another - in this case from the sediment to the overlying water and vice versa. Since a portion of the marsh was also to be returned to the laboratory for detailed study, it was desirable to have the experience of other such attempts before proceeding.

Not only was the literature review limited in scope but also in time. Since the project period was relatively short and most of the effort was expended in the experimental work, the effort available for the literature review did not permit an exhaustive search of the pertinent literature. Yet, the work reviewed and cited herein constitutes the best and more reliable of the previous work as far as the authors could determine.

NUTRIENT EXCHANGE STUDIES

Exchange With Sediments

Introduction

The biogeochemical cycling of nutrients in the marsh ecosystem is a subject of vast complexity. It is well known that the primary productivity of marshes is quite high compared to most terrestrial communities (Odum, 1959), and an integral part of this phenomenon is the cycling of nutrients, primarily carbon, nitrogen and phosphorus. The identification of nutrient sources and sinks and the quantification of rates of exchange between the two are imperative to a thorough understanding of the system. In addition, effects of controlling and/or limiting factors (e.g. temperature, salinity, season, pH, redox potentials, water and sediment chemical characteristics, etc.) on rates of exchange should be considered.

Two important sources and sinks for nutrients are the sediments with
their own peculiar biogeochemical characteristics and the overlying water
column. Interactions between the two are exceedingly complex and hence
have been the subject of numerous investigations. Conceptual models of
internal pools and pathways of exchange between these two pools have
been suggested (e.g. Fenchel, et al., 1973).

Phosphorus

Phosphorus exists in various states: (1) as minerals, primarily apatite,
sorbed to the surfaces of other minerals; (2) in solution in the interstitial
waters of most sediments; and (3) as organic phosphorus in dissolved form or
in detrital and protoplasmic pools (Porcella, et al., 1970). The exchange
of phosphate between water and sediments in natural systems is a complex
process involving not only physico-chemical reactions, but also biological
processes. The controversy concerning the degree of importance ascribed
to the latter has been reviewed by Pomeroy, et al. (1965).

An investigation of phosphate exchange between shaken bottom sediments
and lake water led Olsen (1958) to the conclusion that biological processes
were relatively unimportant, amounting to 5 percent or less of the total flux.
Hayes and Phillips (1958) on the other hand, employing both cores and shaken
sediments, found exchange rates to be reduced by competing bacteria tying
up a significant amount of phosphate in a protoplasmic pool. Pomeroy, et al.
(1965) found that the rates of exchange in core samples were not significantly
different from unpoisoned samples. In suspended sediment experiments,
biological eschange may move nearly as much phosphorus as physico-chemical
exchange with clay minerals. These investigators suggest that in their core
samples, bacterial populations were primarily restricted to interstitial waters.
Any bacterial effects would therefore be minimized due to comparatively slow
rates of diffusion into the undisturbed water column above. The bacterial
populations characteristic of the experiments of Hayes and Phillips (1958)
were active in the water overlying undisturbed cores as well, removing
phosphate from the water itself and reducing loss to the sediments.

Other biological phenomena may influence rates of phosphorus exchange
with the sediments. The effects of both micro- and macroflora and fauna
should be considered. Among these are mixing, translocation, and other
modifications of sediments by burrowing species (e.g. annelids); consump-
tion, assimilation and excretion of nutrients; production of gases; alterations

of chemical and physical conditions (e.g. pH); and others. In experiments on algal growth with sediments serving as the sole source of phosphorus, Porcella et al. (1970) found that soluble orthophosphate was accumulated immediately by the algae and utilized for growth. Using radioactive phosphorus, Pomeroy (1963) found rapid turnover rates of phosphate in coastal waters of from one to seventy hours. Odum et al. (1958) found uptake rates of ^{32}P by marine benthic algae exposed to light to be similar to those maintained in dark conditions in a given tissue. Similar results were found by Teal (1962) in blue-green algae of a Georgia salt marsh. "Luxury consumption" of nutrients from sediments has been shown in emergent aquatic plants in addition to their release of phosphates to the water column (McRoy and Barsdate, 1970).

The exchange of phosphorus between the water column and sediments is governed in part by physical and chemical conditions. Maximum sorption of phosphate occurs when pH is neutral or slightly acidic, with a rapid decrease in percent P sorbed above and below this range (Wentz and Lee, 1969). These investigators found that drying of the sediment increases phosphate availability. Anaerobic conditions with accompanhing lower redox potentials and lower pH values has been found to solubilize more phosphorus than under oxidizing conditions (Mortimer, 1941 and 1942). Organic matter serving as a substrate for anaerobic bacteria can lower pH causing enhanced solubilization of phosphate (Porcella, et al., 1970). The effects of hydrogen sulfide production on inorganic phosphate release from the sediments have likewise been explored (Gooch, 1968).

The geological and chemical properties of the sediments themselves are integral to the inevestigation of exchanges of nutrients. Obviously, sediments of higher silt and clay fractions are a greater source of phosphorus than, for example, sandy sediments (Pomeroy, et al., 1965). The porosity and permeability of sediments affect the nature and degree of exchange. Flow rates, tidal amplitudes, channelization, scour, aeration, mixing and turbidity in the marsh are all important factors which influence exchange rates. The actual depth of the sediment which is involved in exchange processes is a matter of some controversy; this also is of course dependent to some degree on the geological and biological structure of the sediments involved.

Laboratory investigations of the exchange of phosphorus between sediments and overlying waters have involved at least four primary techniques:

(1) slurry tests involving agitation of known concentrations of sediments suspended in known volumes of water; (2) fixed-bed experiments involving undisturbed or semi-disturbed cores with an overlying water column; (3) microcosm analyses involving either steady-state or continuous flow systems; and (4) continuous flow through integral or differential beds.

In these studies, both sorption and desorption of phosphorus from the sediment and/or the water column were followed through various lengths of time and under different conditions. Some of these experiments have been alluded to previously. Pomeroy, et al. (1965), for example, employed both slurry tests and fixed-bed, undisturbed sediment studies. From slurry experiments these investigators determined that at least two very rapid processes were involved, one with a half-life of fifteen seconds or less and the other of approximately fifteen minutes. Influence of biological activity on this kind of technique was highly significant. Fixed-bed tests, on the other hand, disclosed a much slower leaching rate independent of biological activity. An equilibrium in the fixed-bed cores seems to have been achieved after about forty hours. Tests continued after this time showed no additional effects. Similar findings are documented by the works of Keup, et al. (1970) and others.

Uptake or sorption processes have been similarly investigated. A measurable phosphate-solids sorption reaction could not be determined in studies on Chesapeake Bay waters and sediments (Carritt and Goodgal, 1954). These findings complement those of Pomeroy (1963). Although Gessner (1960) found adsorption of phosphate on sediments with increasing water concentrations, all of these investigations seem to agree that sediments in situ act as a buffer on the concentrations of phosphate in the water column.

Continuous-flow microcosms seem to have been designed to study primarily biological processes coupled with manipulation of environmental factors. Continuous flow differential or integral bed techniques have been developed for investigation of solid adsorbents in conjunction with wastewater treatment (Winkler and Thodos, 1971; Gangoli and Thodos, 1973). The later experiments are interesting in that equilibrium relationships and Freundlich-type isotherms are employed in data analysis.

It appears that more detailed investigations of the various factors involved in the exchange of phosphorus between sediments and overlying waters would be useful, not only to define the exact sources and sinks of this nutrient, but also, to establish the exchange rates between these various sources and sinks under simulated natural environmental conditions.

Nitrogen

Laboratory investigations concerning leaching and uptake of nitrogen compounds were found to be sparse. Most experiments have been concerned with biological activities involving uptake and release of varying nitrogen species in the nitrogen cycle. Rates of nitrogen fixation by epiphytes on sea grasses have been reported (Goering and Parker, 1972). Stewart (1969) explored aspects of nitrogen fixation by free-living microorganisms. Regeneration rates of nitrogen and soluble phosphates accompanying decay of aquatic weeds were investigated by Jewell (1971). In these experiments, particle size of detrital materials was shown to affect rates of decomposition and nutrient regeneration. Fixed-bed experiments were performed by Keup, et al. (1970) monitoring ammonia, nitrate, and organic nitrogen leached from various types of soils. Only total nitrogen levels are reported, however, and little conclusive results were obtained.

Rates of organic N sedimentation, exchange rates of ammonia, nitrate, nitrite, and elemental nitrogen denitrification and fixation rates of exchange with biological pools need intensive study.

Exchange With Marsh Plants

Carbon

The coastal marshes that develop along the periphery of Texas estuaries represent a significant contributor of fixed carbon (organic matter) into the nearby estuarine waters. Approximately one-half of the annual marsh production is exported to estuaries. Teal (1962) estimated that 45 percent of Georgia _Spartina_ marsh production is exported into surrounding aquatic systems, while Day, et al. (1972) found that 51 percent of marsh-produced organics enter Louisiana estuarine and coastal waters. This carbon is transported out of the marshes directly as dissolved organic substances, fine organic particles, or detritus, and indirectly as biomass of the numerous secondary consumers (fish, mollusks, crustaceans) that feed in the marsh as juveniles and migrate back to estuarine systems during maturity.

Fragments from decomposition of _Spartina_ grasses and algal mats and fecal material from marsh consumers (amphipods to _Nutria_) contribute to the tremendous amount of organic matter that supports estuarine detritus-based foodwebs. Armstrong and Hinson (1973) estimated that daily production from 55.2 sq mi of marsh around Galveston Bay, Texas introduced more organic

matter into this system than waste discharges and river inflow combined, while phytoplankton production in the entire Bay was 25 times greater.

Odum, Zieman, and Heald (1973) characterized the degradation of macrophyte bascular plants to detritus particles as a three-step process: (1) loss of soluble compounds shortly after death; (2) microbial colonization (bacteria and fungus); and (3) mechanical fragmentation of the more resistant tissue.

The loss of soluble organic components within the dead plant tissue generally occurs within a few days and can proceed while the leaves and stems are still upright in the marsh. Up to 25 percent of the initial dry weight may be lost during the first stage of degradation (Odum et al., 1973). The amount of this soluble material for transport out of the marsh is supplemented by the products of the relatively-easy decomposition process for marsh benthic and epiphytic algae. Since marsh algae are subjected to rapid dessication during periods of low tide or reduced river inflow, the dead algae can release significant amounts of soluble organics (sugars, organic acids, etc.) during subsequent inundations. Indeed, Gallagher and Daiber (1974) found that gross algal production was about one-third of the net production for vascular plants in a Delaware salt marsh.

The solubilization of dead plant tissue may be facilitated by saphrophytic fungi. Gessner, Goos, and Sieburth (1972) found that the internodes of lower stems and leaves (submerged) of <u>Spartina alterniflora</u> were colonized by mycelium of the fungus, <u>Sphaerulina pedicellata</u>. Sexual stages of this fungus developed rapidly as the plants senesced in the late summer and fall. The fungal biomass served as a source of nutrients for other microorganisms and resident consumers (nematodes and mites).

The availability of soluble organic decomposition products leads to a rapid proliferation of microbes on the dead <u>Spartina</u> leaves. Burkholder and Bornside (1957) found numerous aerobic, heterotrophic bacteria that actively help to decompose <u>Spartina</u> and estimated that 11 percent of the annual marsh crop was converted to bacterial biomass. Their work with decomposition of <u>Spartina</u> leaves submerged in litter boxes showed that all but the most resistant stems of these marsh plants were decomposed within six months. The microbial activity proceeds rapidly on the protein and carbohydrate fractions, but the more resistant cellulose and lignin fibers of aquatic macrophytes may remain in the sediments for many months (Jewell, 1971). Conversion of decomposition products by microbes into

more stable organic molecules (i.e. branched chain fatty acids), has been noted (Schultz and Quinn, 1973), and these products often remain in marsh sediments for some time.

Fragmentation of decomposing leaves occurs due to wind and tidal action, water currents, and the feeding activities of marsh animals (both terrestrial and aquatic). Fenchel (1972) found that Thalassia detritus passed through the guts of amphipods unchanged. Apparently, these microcrustaceans ingest only the bacteria associated with plant fragments, but mechanically grind the detritus into smaller particles. Jewell (1971) found that single fragmentation and breakage did represent a significant detritus-forming mechanism for aquatic macrophyte systems.

Phosphorus

The phosphorus cycle in marsh and marine seagrass ecosystems has been studied extensively (Pomeroy, 1959; McRoy and Barsdate, 1970; McRoy, Barsdate, and Nebert, 1972). According to Pomeroy, et al. (1972), "there is no evidence that phosphorus ever is limiting to the productivity of the estuaries of the Southeastern U. S." If one assumes that Texas estuaries function similarly to these shallow, turbid bays along the Georgia coast, normal exchange processes would seem to be rapid enough to prevent depletion. The relatively constant aqueous levels result from the rapid reestablishment of phosphorus equilibrium between water and suspended sediments due to biological exchange and physical sorption mechanisms (Pomeroy, et al., 1965).

The mechanisms of phosphorus exchange with vascular plants differ somewhat between the constantly submerged species and emergent species. Emergent plant species, such as Spartina, are exposed to changing water levels where the amount of direct contact with the water is variable. Box and Chamrad (1966) describe the biome occupied by a pure strand of Gulf cordgrass (Spartina spartinae) in south Texas as being a stable climax condition. The distribution of this common marshgrass is apparently edaphically controlled, i.e. related to soil properties, such as salinity, nutrient content, alkalinity, and drainage. This relationship to soil type and content is important to nutrient cycling, since Pomeroy, et al. (1972) found that Spartina removes all or most of its subsurface sediments.

Blum (1969) advanced the hypothesis that the structure of Spartina patens clumps (both living and decomposing leaves) acted as a fine mesh that traps and removes nutrients during period of inundation. Depressed

total phosphorus levels were found when flooding of the upper marsh by high spring tides reached its peak. However, this drop in phosphorus content resulted from dilution of phosphorus-rich waters around the Spartina vegetation, rather than uptake by the extensive mesh of plant stems.

Completely-submerged marine grasses, such as Zostera (Alaska) were shown to take up phosphate through both leaves and roots, although the direction of transport can be reversed when external concentrations decrease (McRoy and Barsdate, 1970). Patriquin (1972) found a similar pathway for Thalassia (the typical seagrass in Texas estuaries) and estimated that the available phosphate (interstitial and adsorbed) in the root layer sediments constituted a 300 to 1000 day supply. Furthermore, he determined that the nutrients which maintain the root layer supply are indigenous and do not come from regeneration of organic matter deposited in sediments or diffusion through the sediment-water interface. Excretion of phosphorus by most marsh and seagrasses occurs due to excessive uptake from the phosphorus-rich sediments and subsequent release into surrounding waters.

According to the previously described mechanisms, phosphorus exchange for Spartina begins with absorption of soluble sedimentary phosphorus by roots and rhizomes, becomes incorporated in the plant biomass, and is returned to the water by the leaves (generally as particulate phosphorus). Soluble and particulate phosphorus excreted by the vascular plants is available to epiphytic and benthic algae, which are primarily responsible for removing phosphate from the marsh waters (Pomeroy, et al., 1972).

Nitrogen

The nitrogen cycle in a Spartina marsh seems to be based on the decomposition of senescent vegetation. The proteinaceous component of cordgrass is quickly converted to organic nitrogen and then deaminated to produce ammonia. Ammonia is oxidized to produce nitrite and finally the stable, aqueous form, nitrate.

Rooted plants can utilize the ammonia, nitrite, and nitrate in the sediments (interstitial water) or surface waters for production of additional biomass. However, the available supply of nitrogen is much less than observed for phosphorus, and could well become limiting to plant growth. Patriquin (1972) reported that the available supply of inorganic nitrogen in a Thalassia bed could only support 5 to 15 days growth – less than 1 percent of the in situ phosphorus supply

A valuable source of inorganic nitrogen for macrophyte growth appears
to be the nitrogen (N_2) fixed by blue-green periphyton which grow on the
submerged leaves and stems or on the sediment surface as algal mats.
Patriquin (1972) and Goering and Parker (1972) both concluded that nitrogen
fixation was essential to submerged marine grasses. Nitrogen fixation by
bacteria may also occur in sediments with high reduction potential, where
organics released by plant roots are utilized by N-fixing bacteria which
in turn release ammonia needed for plant growth.

MODEL MARSH ECOSYSTEMS

Spartina-Based Microcosms

The vast majority of marsh-related studies are conducted in the field;
however, it is also practical to remove a portion of that biome and transfer
it to the laboratory for controlled experimentation. Nadeau and Roush (1973)
utilized a saltmarsh microcosm to demonstrate the impact of an oil spill on
a marsh community. Their large model ecosystem (4 x 5 feet) contained
intact sod sections of both Spartina alterniflora and S. patens, snails, and
fiddler crabs. Water level was maintained at high tide level and did not
fluctuate. These investigators used growth of the marsh plants in the
microcosm unit and at the original marsh site as the comparative variables,
but found no significant difference during the growing season. They did note
that normal salinity and tidal regimes were essential for optimum growth
of these marsh macrophytes in microcosms. Spilled oil did not adversely
affect the marsh grasses, since it degraded on the surface of submerged
leaves and sediment without incorporation into the plants themselves.

The Nadeau and Roush study (1973) appears to be the first attempt at
using a Spartina-dominant community in the lab for experimental purposes.
However, the epiphytic and benthic algae present on the partially-submerged
Spartina alterniflora were not monitored, even though they are known to
contribute substantially to total marsh productivity. In order to accurately
simulate an inundated marsh area, the algal component must be analyzed
since it responds directly to water quality parameters (nutrients, toxic
substances, etc.).

Algal Microcosms

Because the Aufwuchs mat community that commonly develops in micro-
cosms closely resembles those algal mats common in Lavaca Bay marshes,

this discussion will include some pertinent observations relating to microcosm algae and nutrient exchange processes. Investigations using saline micro-cosms (simulations of estuaries) include Abbott (1967), Cooper (1970), and Armstrong and Hinson (1973). Porcella, Kumagai, and Middlebrooks (1970) used an experimental setup very similar to that used in this study, although they were looking at the exchange of phosphorus between freshwater and lake sediments.

Abbott (1967) tested the effect of single doses of phosphate (1-100 micro-moles/l) and nitrate (10-100 μ moles/l) on the autotrophic algal community in estuarine carboy microcosms. He observed that each macronutrient stimulated production independently, and that mixtures did not produce substantially higher community metabolism rates. Apparently, the micro-cosm algae produced luxuriant mats when nutrient levels were high and maintained their large biomass even when concentrations were very low and no further inputs were made.

Cooper (1970) found that microcosm algal production actually increased when freshwater inputs were cut off during "drought" simulation in his continuous-series Trinity Bay microecosystems. Although actual nutrient concentrations were not monitored, the production increase appears to occur in spite of the lack of potential nutrient input (in the freshwater). However, the algal mats in successionally-advanced microcosm communities appear to be nutrient-starved and are capable of rapid uptake of added nutrients with little observed production increase (Armstrong and Hinson, 1973; Hinson, 1974). Flushing of these nutrient-depleted microcosms (very low nitrogen and normal phosphorus) with nutrient-free water did spur additional algal growth and production in those systems (models of Galveston Bay) not limited by other water quality parameters (i.e. wastewater toxicity). Nutrient inputs, especially nitrogen, are rapidly removed from microcosm waters by the algal mats and converted to additional algal biomass.

For their Plexiglass reactors containing sediment, algal mat, and over-lying freshwater, Porcella, et al. (1970) determined that "the soluble ortho-phosphate is accumulated immediately by the algae and then utilized for growth." Phosphorus exchange with the sediments probably relates to the extensive microbial and algal activities at the sediment-water interface and within the top few centimeters of the lake sediments.

CHAPTER III

METHODS USED

NATURE OF STUDIES CONDUCTED

Two major types of studies were conducted during the course of this project. First, field investigations were carried out to assess the movement of tidal waters into and out of the marsh system and the accompanying mass flows of carbon, nitrogen, and phosphorus. From these studies, it was anticipated that exchange rates of nutrients from the marshes to the surrounding bays could be determined. Along with these nutrient mass flow estimates, measurements were made of other water quality parameters, such as dissolved oxygen and pH, to determine the natural fluctuations of these parameters as well as the computation of community productivity and respiration.

The other studies in this project were performed in the laboratory to delineate in more detail the exchange rates of nutrients from marsh sediments. Three types of tests were performed to determine these rates: slurry tests using a suspension of sediments obtained from the marsh system; fixed-bed tests using cores of sediment from the marsh system; and reactor tests in which a portion of the intact marsh system was brought into the laboratory for nutrient exchange tests.

FIELD INVESTIGATIONS

Sampling and Sample Analysis Procedures

Sampling Stations

A total of five sampling stations were utilized at various times during the summer field program (see Figure III-1 for map with marsh station locations). Four stations were located along the major bayou and its tributaries that drain the extensive marshes on the peninsula between Swan Lake and the Lavaca River. The other sampling site, Station 5, was established in Swan Lake approximately 100 feet from the mouth of the main bayou, but measurements here were restricted to those times during the second field trip when a boat was available. Sampling at this point in the four-foot deep Swan Lake was used to verify that the water entering the marsh during flood tide did come from the Swan Lake "reservoir".

Figure III - 1

LOCATION OF SWAN LAKE
MARSH STATIONS

SWAN
LAKE

x 5

Ⓐ

2

1

3

Ⓑ

Ⓒ 4

Scale: 1" = 280'

A - B = 1120'
B - C = 220'
C - D = 890'

Station site: ▬

Ⓓ

"Large pond"
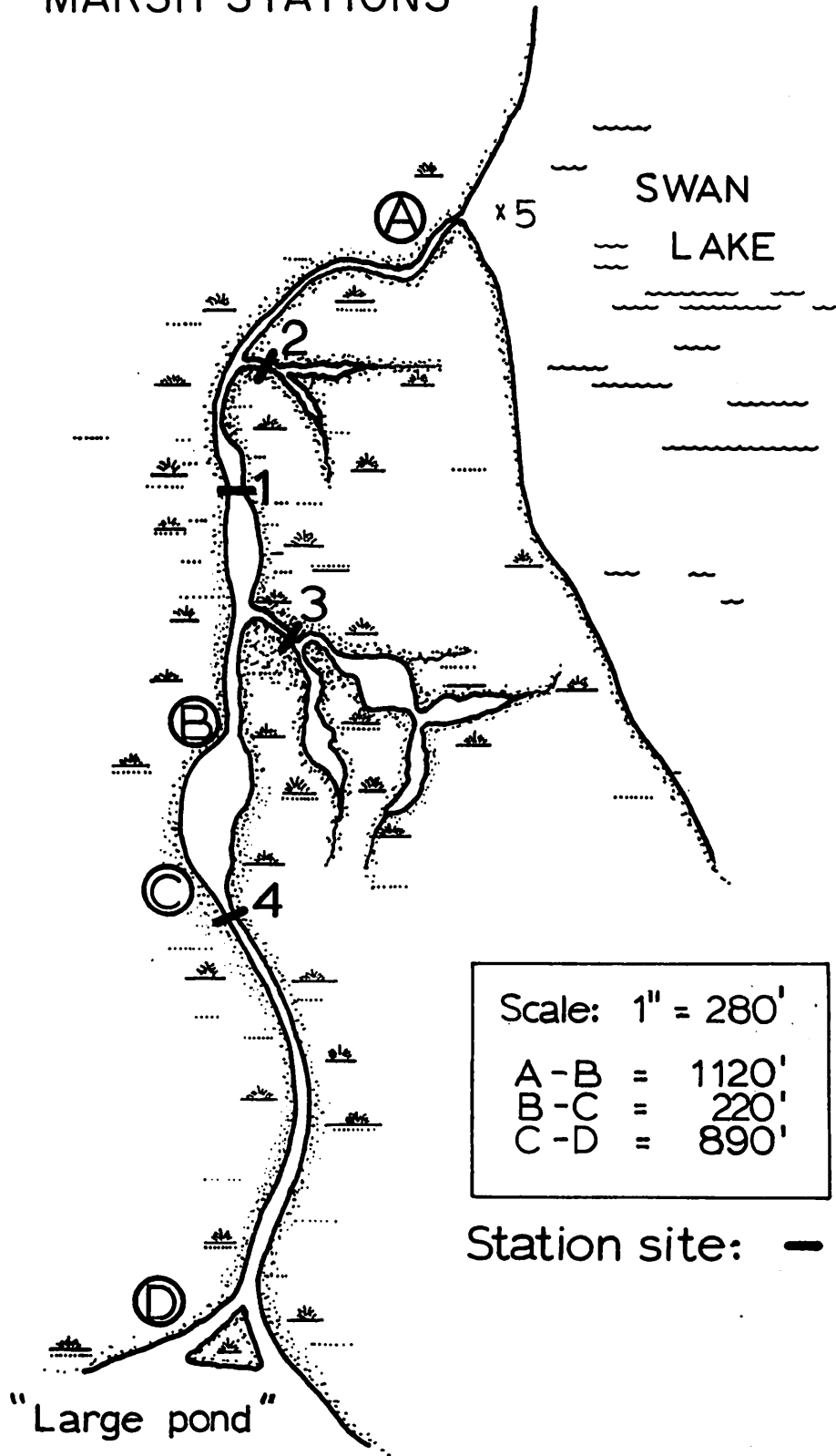
Station 1 was located on a well-defined section of the major marsh bayou where the channel sidewalls are steep and distinct and the entire bed is composed of smooth clay scoured by rapid water movements. Here the bayou is 12 feet wide and 2 to 3 feet deep, depending on the prevailing tide stage. Figure III-2 illustrates the channel cross-sections at the various marsh sites, including Station 1. Since a temporary bridge spanned the bayou at each station, water samples, flow measurements, and other water quality parameters could be taken at the exact same point each time. These sampling points were determined by a preliminary stream rating which revealed the particular location where water movement approximated the average water velocity for the entire stream profile.

Station 2 was established on a small feeder channel that enters the main bayou between Station 1 and Swan Lake. However, this small and shallow (less than one foot deep) channel was abandoned after the first field trip when it became apparent that even a slight drop in overall water level would leave no water in the channel and completely isolate the algal mat potholes that it drained. In addition, water entering this portion of the marsh during a flooding tide completely overflowed this small channel and entered through other ill-defined channels, thereby making accurate determination of total water influx impossible.

Station 3 was established on a small distinct bayou that drains a substantial vegetated area and a series of algae-rich potholes between the major bayou and Swan Lake. The cross-section at this point is essentially U-shaped with a 3-foot width and a maximum depth of 1.5 feet. A flooding tide often caused water to infiltrate into the marsh along the Swan Lake shoreline, flow through this channel, and supplement the water moving into the back reaches of the marsh upstream of the main bayou channel. This small channel did empty completely at the sampling site during the third field trip when a long slack tide was coupled with overall low water conditions.

Station 4 was situated on the main bayou channel after it narrows "downstream" from a large pothole (see Figure III-1 for map details). From this sampling site, the channel continues toward a large bi-lobed pond and extensive slightly-vegetated mudflats which serve as the alternate water reservoir for the main bayou with its oscillating-flow characteristics. The bayou cross-section at this station had nearly the same dimensions as Station 1 (refer to Figure III-2). Measurements at this station began on the second

Figure III-2

BAYOU CROSS-SECTION AT SWAN LAKE MARSH STATIONS

STATION I.

2.60 ft

STATION 2.

0.75 ft

STATION 3.

1.38 ft

STATION 4.

2.00 ft

SCALE: 1/2" = 1'

0   1   2   3   4   5
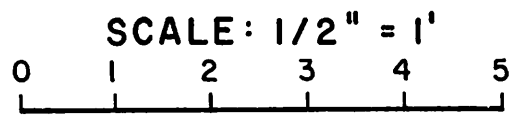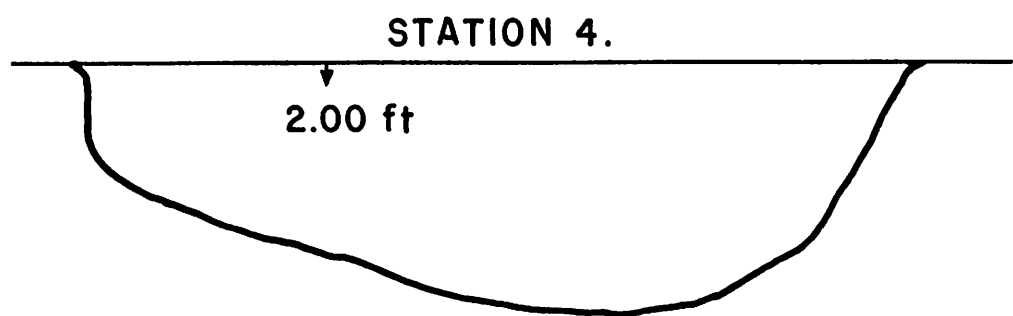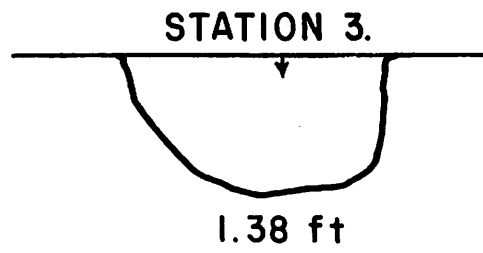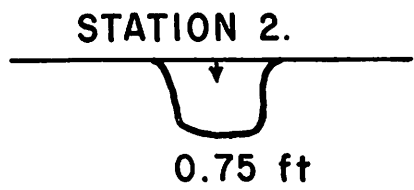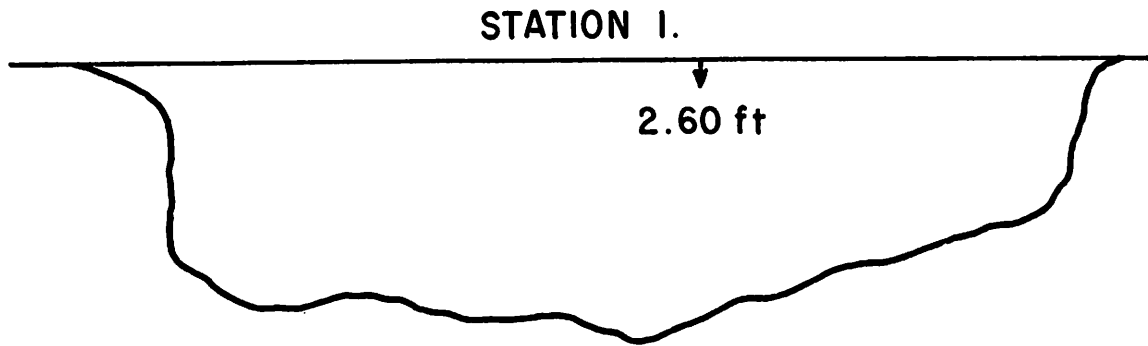
↓ SAMPLING POINT
(2.00) DEPTH AT SAMPLING POINT

field trip to quantify the contributions of the back marsh areas which exhibit the most extreme variations in exposure and inundation.

Measurement of Hydrologic Parameters

Flow measurements were taken with a manually-held Pygmy meter #R-720. Velocity in feet per second is calculated from the number of revolutions of the meter cone wheel that occur in 40-70 seconds. Each revolution produces an audible click in the headset, and these clicks are counted by the operator during the allotted period (monitored with a stopwatch). For this particular meter, velocity data are obtained through the use of the following standard equation:

$$V = 0.956 \ N + 0.04 \tag{III-1}$$

where:

N = Revolutions of the wheel (number per second)

V = Velocity (fps)

Field velocity measurements are taken at 0.2, 0.6, and 0.8 total depth for a representative sampling point. The actual depth of measurement changed as water depth fluctuated. The sampling point at each station was determined by constructing a complete velocity profile for the bayou cross-section and selecting the channel section (1 foot wide) that exhibits water velocities closest to the entire stream mean velocity. See Figure III-2 for the bayou cross-section at the field stations and location of flow measurement sites.

Water depth at the representative sampling points was taken regularly with the Pygmy meter staff which is marked with 0.1 foot graduations. These data provide a continual picture of relative tidal effects on the actual marsh area, even though the TWDB tide stage gauges located nearby in Swan Lake give rated delineation of tidal amplitude.

Measurement of Water Quality Parameters

During the field sampling, physical water quality parameters, such as temperature, pH, conductivity, and dissolved oxygen, were monitored in situ at the various marsh stations. The dissolved oxygen levels were measured with a YSI model 51A Oxygen Meter that has manual temperature and salinity compensation. The probe is submerged about one foot into the bayou waters and moved continually to insure stable readings. Both air and water temperature ($^{\circ}C$) were measured using the thermistor in the

oxygen probe during the normal oxygen procedure. Readings were taken at the same point in the bayou cross-section as the flow measurements.

A portable Beckman pH Meter was used to monitor pH. Grab samples of the marsh water were collected in glass bottles and run immediately after sampling all field stations. A Beckman conductivity meter was available for some sampling periods during the second and third field trips, but the conductivity data were not continuous. Readings of conductance were taken in situ by inserting the large electrode unit directly into the bayou waters.

Water samples for laboratory analyses were collected approximately six inches below the water surface when water depth permitted. All water samples are essentially surface grab samples - taken to exclude organic surface films. Bulk samples were normally collected in new one quart Cubitainers*, although acid-cleaned glass bottles were used during the first field trip.

Analyses for carbon content of the marsh waters were performed at the Center for Research in Water Resources laboratory following each field trip. Both total organic carbon (TOC) and volatile suspended solids (VSS) were measured to show the relative proportion of dissolved and particulate carbon. TOC samples were collected in 50-ml Nalgene vials and stored on ice with no preservative added. Upon return from the field, these samples were stored in a $4^{o}C$ cold room until they could be run on a Beckman Total Organic Carbon Analyzer Model 915. Injected samples yielded estimates of total carbon and inorganic carbon, and the difference represented the TOC content. All TOC measurements were completed within two days of returning.

The determination of volatile suspended solids (labile particulate organic component) required a different procedure than TOC. A 100-ml water sample was removed from the phosphorus Cubitainer (preserved with chloroform) after it was vigorously shaken. This water was vacuum-filtered through RA glass fiber filters (tarred). The resultant filter containing the particulate component (wet weight) was dessicated overnight in a $100^{o}C$ oven. The filter was reweighed to obtain the dry weight, and then the organic matter was combusted in a furnace at $550^{o}C$ for 20 minutes. The difference between dry and combusted weights represented the VSS fraction.

---

*Hedwin Corporation Cubitainers

Phosphorus samples were collected in the quart-size Cubitainers and preserved : by the addition of 2 ml chloroform to stop biological degradation and nutrient regeneration. The bulk samples, after removal of 100 ml for VSS analysis, were stored in a $4^{\circ}C$ cold room until delivery to the State Health Department Laboratory for analysis of total phosphorus and orthophosphorus content. Nitrogen samples were handled the same way, except that 2 ml of concentration sulfuric acid (36N) was used as preservative. The State Health Department Laboratory analyzed for organic nitrogen, ammonia, nitrite, and nitrate to reveal the complete series of aqueous nitrogen forms. Refrigeration of bulk samples took place only after return to the laboratory.

Methodology for Data Analysis

Hydrologic Parameters

Since the marsh bayou acted as an oscillating stream system, capable of switching the direction of water flow, it was important to know the sources of the waters in the bayou, that is, whether the water moving through the bayou monitored could have come from Swan Lake or the standing waters of the upstream marsh. This hydrologic parameter was obtained by calculating the cumulative distance traveled by a single water mass during the period of measurement which was over at least one tidal cycle. The period of measurement was divided into time intervals, Δt, and the distance, r, that a water mass would travel in that time interval was calculated as:

$$r = v \cdot \Delta t \qquad (III-2)$$

where v was the average velocity of the water during the time period. Cumulative sums were computed for the total distance traversed by the water mass from the start of the measurement period to the end of that period. Plots of the cumulative distance traveled revealed the total distance upstream and downstream that a water mass would have moved over the measurement period and thus whether water from Swan Lake, for example, could have reached Stations 1 or 4 during the tidal cycle.

Additional hydrologic data on the quantity of water movement was essential for subsequent analyses of material flows (nutrients). The mass flow of marsh water through each station (in cfs) was calculated by multiplying the average water velocity by the cross-sectional area of the stream

channel. Changes in channel area occurred in response to changing tidal amplitude (stage differences), but the appropriate increase or decrease in area area was utilized when calculating the actual water flow.

Water Quality Parameters

Changes in the quality and quantity of carbon, nitrogen, and phosphorus were analyzed to determine the mass nutrient exchange between the marsh and adjacent estuarine waters (Swan Lake). Variation in the ambient concentration of each nutrient species was monitored over both ebb and flood tides. Hydrologic effects on nutrient concentrations were revealed by plotting nutrient levels during an entire 24-hour study period (at least one complete tide cycle).

Since the volume of water moving through each station was known, determination of nutrient mass flows only required the quantity of nutrient mass (per unit volume) in the marsh water. Mass flows during both flood (entering marsh) and ebb (leaving marsh) periods were compared to illustrate the overall mass balance, and this difference was indicative of the marsh's role as source or sink for the particular substance.

LABORATORY INVESTIGATIONS

Introduction

In order to investigate the magnitude and nature of exchange rates of nutrients between marsh sediments and the water column, three basic experimental techniques were employed: (1) slurry tests simulating conditions of extreme mixing; (2) fixed-bed tests simulating calm to slight conditions of agitation; and (3) reactor tests simulating natural continuous-flow conditions through different marsh communities. In each of these experiments, environmental conditions of temperature, salinity, and nutrient levels were controlled at different levels. In addition, in each experiment an effort was made to determine both uptake and release of nutrients by the sediment and its associated flora and fauna by varying nutrient concentrations in the water column. In order to more closely approach a natural situation, no poisoning of samples was attempted.

In the sediment sorption investigations, extractions of sediment interstitial waters were not completed, but analyses of nutrient concentrations in the water column were carried out. With this procedure, some idea could

be gleaned concerning the processes predominantly involved in exchanges between the various sources and sinks in the experimental systems. In all experiments, samples of water were analyzed for ammonia, nitrate, and orthophosphate at the Texas State Department of Health Laboratory. Ammonia was determined utilizing a specific ion electrode followed by a distillation and direct Nesslerization. Nitrate analyses were performed using the brucine method, and orthophosphate was analyzed using the ascorbic acid method, both according to procedures set forth in <u>Standard Methods</u> (1971).

In the reactor experiments, organic nitrogen, ammonia, nitrite, nitrate and total phosphate were measured; supplemental measurements of TSS, VSS, and TOC were made for many of the experiments. Diurnal changes in pH, temperature, and dissolved oxygen were closely monitored in the reactors during the experiments. All samples taken for nutrient analyses were quickly preserved using either concentrated sulfuric acid or chloroform in accordance with <u>Standard Methods</u> (1971) and kept at $4^\circ C$ until analyses could be performed.

Slurry Tests

During the first field trip, samples of sediment were collected from the marsh and transported to the laboratory where they were stored at $4^\circ C$ until experiments commenced. A sample of sediment was removed at the beginning of these experiments and sent to the Texas A&M University Soil Testing Laboratory for detailed soil analysis. Analyses of sediment samples revealed that they were approximately 67 percent interstitial water, 5 percent organic combustible matter, and 28 percent noncombustible material.

The slurry experiments were conducted to define two exchange rates: leaching and uptake. These studies were performed at room temperature (approximately $22^\circ C$) and were duplicated using distilled water and an INSTANT OCEAN* adjusted medium of 20 ppt.

Leaching Tests

Leaching experiments were performed according to the following procedure. Approximately 50 grams of sediment were removed from the $4^\circ C$ room and spread on a glass plate to a thickness of approximately 1 centimeter. An attempt was made to insure a homogeneous mixture by carefully mixing the sediment with a clean spatula. This sample was then allowed to air dry for one hour. At the end of this period, portions were weighed

to obtain the following amounts: 4, 40, 400, and 4000 mg. Each weighed aliquot of sediment was replicated to give three samples of the corresponding weights. Each portion of sediment was then washed into a 500-ml Erlenmeyer flask and covered with 400 ml of of distilled water (0 ppt salinity). Hence, relative concentrations of sediment to water considered were 10, 100, 1000 and 10,000 mg/l. The flasks were sealed with rubber stoppers, attached to a shaker table and violently agitated along with an additional flask containing a distilled water blank.

One flask of each sediment/water concentration was removed at the end of 12, 24, and 72 hours of shaking. Samples were filtered using a spun glass filter (pore size approximately 4 μ) and the filtrate preserved for later analysis of ammonia, nitrate, orthophosphate, inorganic carbon (IC), total carbon (TC), and TOC. The two samples of highest concentration (i.e. 1000 and 10,000 mg/l) were centrifuged at 7,500 RPM for thirty minutes prior to filtration. Although centrifugation removed most of the filtrable fraction of the sediment, a colloidal fraction in the water persisted. This phenomenon has also been noted in the literature and is thought to be due to the disruption of bonding between clay particles by distilled water (Pomeroy, et al., 1967).

Simultaneous daily agitation, centrifugation, and distilled water washing of a large (approximately 100 mg) aliquot of sediment was conducted for subsequent uptake experiments. Ten washes were conducted in this manner, and at the end of the period the supernatant water was filtered and nutrient analyses performed on the filtrate. Pomeroy, et al (1965) found that nine distilled water washings of Georgian estuary sediment showed only slight reduction in the mass of phosphate removed (averaging 4.7 μg P/gram of sediment) with each successive wash.

Leaching experiments at 20 ppt were performed in a like manner. Distilled water dilutions of full strength INSTANT OCEAN* were made to achieve a salinity of 20 ppt. Blanks were analyzed before and after the experiments, and it was found that nutrient levels in INSTANT OCEAN* preparations varied considerably as did those of the distilled water blanks.

Uptake Tests

Sediment washed with distilled water was centrifuged following the tenth wash, removed, and air dried for one hour in preparation for the uptake experiments. The effects of successive centrifugation and washing on the

integrity of the sediment was of some concern. Not only was a colloidal fraction lost with each washing, but also a goodly portion of organic and other matter of low density not retained by centrifuging. Furthermore, effects on any organisms inhabiting the sediments should be considerable.

Aliquots of sediment and volumes of water were the same as in the leaching experiments. Distilled water (0 ppt salinity) was spiked with nutrients (ammonium chloride and monobasic potassium phosphate) to achieve a solution containing 5 mg NH_4-N/liter and 2 mg PO_4-P/liter respectively. Appropriate flasks were removed and their contents centrifuged, filtered and preserved for subsequent analysis of nutrients. Time intervals were lengthened for these experiments such that samples were taken after 24, 48, and 120 hours. Sorption processes, particularly for phosphates, are known to proceed at a rate much more slowly than desorption. By lengthening the contact time, a better estimation of rates of exchange could be determined. Slurry uptake tests were repeated using spiked water with a salinity of 20 ppt.

In none of the above preliminary tests were pH values checked; this was unfortunate in view of the fact that many sorption rates of exchange can be highly correlated with changes in pH. However, the well known buffering capacity of seawater may have limited changes in pH.

Data Analysis

In order to establish exchange rates between suspended sediments and overlying water, the following model was employed:

$$\frac{dC_w}{dt} = k \, [aC^{1/n} - C_w] \qquad \text{(III-3)}$$

where:

dC_w/dt = rate of change of concentration in the water of a given nutrient through time,

k = mass transfer coefficient,

a, n = constants, and

C = equilibrium concentration of the nutrient in the presence of sediment.

The water-sediment relationship, $x/m = aC^{1/n}$, can be derived by knowing the mass of nutrient sorbed (x), the mass of the sediment (m) and the concentration of the nutrient (C) in the water after equilibrium conditions have been established. By regressing $\ln(x/m)$ on $\ln(c)$, a family of curves with slopes $1/n$ result for each time of successive sampling periods. Freundlich-type

isotherms can be derived, and these in turn can be related to environmental factors (e.g. temperature and salinity). As long as the value of x/m is known then C may be estimated for use in Equation III-3. A similar equation could be developed for nutrient concentrations in sediments to make both the water and the sediment nutrient reservoirs dynamic. For phosphorus at least, it may be possible to assume that x/m is constant, and therefore C would vary only with environmental variable changes.

Rates of exchange, either sorption or desorption, and equilibrium conditions can be quantified and defined for the marsh system under conditions of extreme turbulence. If the mass of sediment suspended in the water column is known during such periods, the preceding model may help predict the sign and the magnitude of the nutrient exchange.

Fixed Bed Tests

On June 28, 1974, core samples were removed from the marsh from the same general area as the sediment for the slurry tests. This area was one of periodic inundation and at the time of sampling was covered with a layer of quiet water to depths of 10-15 cm. Fourteen core samples were taken avoiding areas of intensive algal and emergent macrophyte colonization. Although the cores were taken at random throughout the area, there were noticeable differences in their flora and fauna upon return to the laboratory. Varying numbers of juvenile fish, annelids and crustaceans were noted.

The cores were extracted by pressing 50-cm sections of white PVC pipe with an inside diameter of 10.16 cm into the sediment to give a sediment depth of approximately 25 cm (see Figure III-3). The base of each core was then sealed with a rubber sheet fastened around the pipe by a flexible clamp, and all were returned to the laboratory. The cores were then allowed to sit for three days at room temperature (approximately 22°C) during which time dissolved oxygen was monitored daily. By the afternoon of July 1, all cores had become essentially anaerobic with dissolved oxygen readings of the overlying waters averaging 0.5 mg/l. The original water was removed at this time, carefully noting its volume of water, and analyzed for ammonia, nitrate, and phosphorus. This original volume of water was replaced with distilled water to the same volume except for two cores which had lost a considerable portion of their water. In these, the volume of replacement water was doubled.

The experimental design of the fixed-bed experiments involved a basic draw and refill technique in order to follow processes of leaching and uptake

FIXED.- BED EXCHANGE APPARATUS
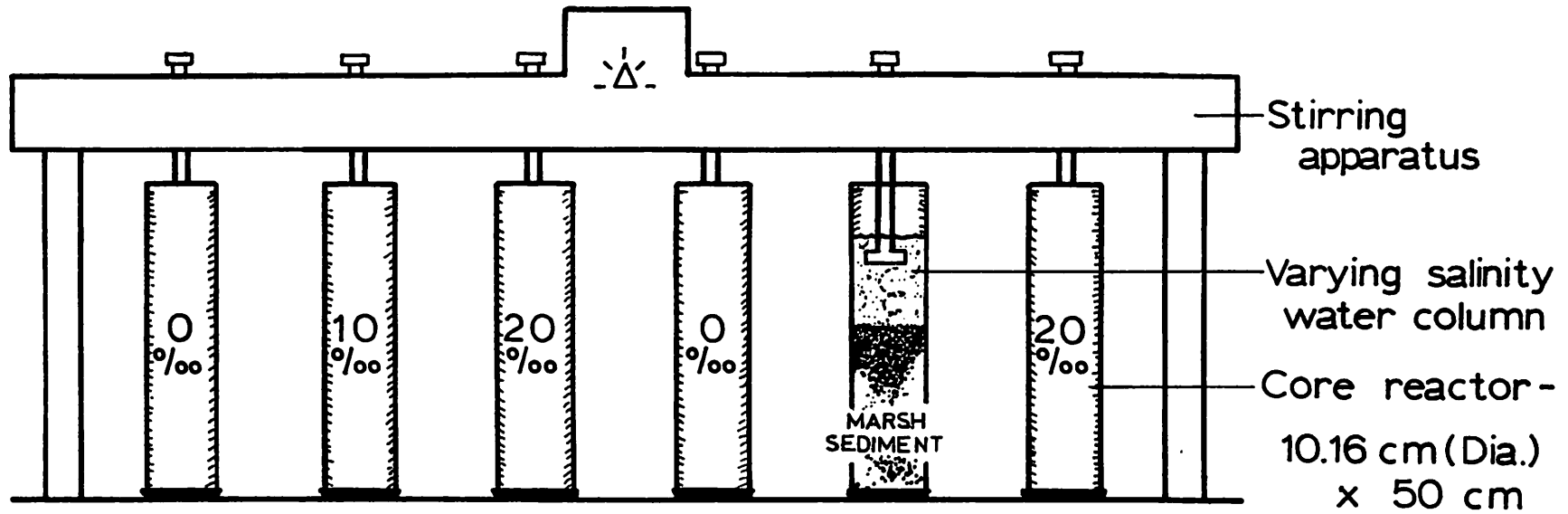
Stirring apparatus

Varying salinity water column

Core reactor-
10.16 cm (Dia.)
× 50 cm

0 ⁰/oo   10 ⁰/oo   20 ⁰/oo   0 ⁰/oo   MARSH SEDIMENT   20 ⁰/oo

Figure III-3

of nutrients. Overlying water was withdrawn using a siphon with the intake as close as possible to the sediment-water interface, but avoiding the removal of the sediment with the sample. Refill was accomplished by gently and slowly pouring the new water down the side of the slightly tilted container. Each refill procedure, however, did disturb the sediment to a certain degree.

These experiments involved three different salinities (0, 10 and 20 ppt) at three different temperatures. Mean water temperatures over the time of sampling were 24.6, 22.5 and $10.1^{\circ}C$. Cores at room temperature were replicated at each salinity. Six cores, therefore, were kept at $22.5^{\circ}C$ (two at each level of salinity) with three cores kept at the high temperature and three at the low temperature. High temperature cores were maintained in an unairconditioned room and were subject to some diurnal temperature fluctuations ($\pm 2.5^{\circ}C$). Cold temperature cores were kept in a thermally regulated water bath. Thus twelve cores were maintained under these conditions and leaching experiments commenced. The two remaining cores were also maintained at room temperature and received uptake water spiked with nutrients for uptake tests as in the slurry tests (5 mg NH_3-N/l and 2 mg PO_4-P/l). One of these cores was covered with distilled water while the other was covered with 10 ppt brackish water.

Both leaching and uptake experiments covered a span of either four or five days with draw and refill taking place every twenty-four hours at 1800 hours. After termination of the first set of experiments, all cores were allowed to sit for three days before the water was removed and analyzed. At this time the procedures were reversed, so that the twelve leached cores each received spiked water for the uptake tests. The two remaining cores at room temperature were simultaneously started on a leaching program. After four days of successive draw and refill procedure, the cores were allowed to sit for twelve days. After that time leaching experiments were again performed on the twelve and uptake on the two for another four day period.

The six cores at room temperature involved in the original leaching studies were each slowly stirred (approximately 14 PRM) by a bank of stirring paddles driven by a variable speed motor. Warm temperature cores were similarly stirred commencing with the second set of experiments. Vibration from the cooling bath stirrer kept the cold temperature cores in a similar state of agitation. Cold temperature cores, however, showed some

signs of temperature stratification and were, therefore, covered with loose fitting caps of styrofoam. Cores at room temperature and high temperature were exposed to a light-dark cycle approximating natural conditions.

After initial replacement of water covering all cores on July 1, the experiments involved draw and refile with all of the three salinity waters. Volumes exchanged were always measured and one liter of replacement water was added each time. Although not all of the water was removed at each draw and refill procedure, the replacement with one liter made the volume remaining comparatively insignificant. Although typical evaporation rates varied for cores at different temperatures, they still exceed any cumulative increase in water volume due to constant conditions.

For the duration of the experiments, dissolved oxygen and temperature of the water columns were checked in the early morning and in the late afternoon prior to draw and refill procedures. The pH was measured only once during experimental procedures. Other parameters were noted in a qualified manner but not quantified (e.g. hydrogen sulfide concentrations and turbidity).

Reactor Tests

The general experimental apparatus for physical marsh simulation is shown in Figure III-4. Figure III-5 depicts an individual marsh reactor. Six plexiglass tubes about 1.8 meters in length and with an inside diameter of 29.3 cm were secured as containers for the marsh microcosm reactors. These tubes were taken to the marsh in mid-July and samples obtained by pressing the tubes into the sediment, removing an intact core, and sealing the base of each tube. Three samples of a typical algal mat community were taken (Reactors 1, 2 and 3) and three of a salt marsh bulrush community (Scirpus maritimus macrostachyus) with healthy emergent plants (Reactors 4, 5 and 6). All samples were taken in the same general area as the previously mentioned cores for fixed-bed experiments. Sediment depths averaged roughly 50 cm. During this trip to the marsh, water was also collected in the 1800 liter boxes shown in Figure III-4.

Upon return to the laboratory, the reactors were placed in a large tank with continuous flowing water as a temperature buffer. They were then fitted with inflow ports about 15 cm above the sediment and outflow ports about 3 to 5 cm above the sediment. These ports were opposingly situated on each reactor to insure proper internal holomixis. Each inflow port was

SCHEMATIC OF CONTINUOUS FLOW REACTOR SYSTEM

Spartina & Algal mat Reactors (6) [29.3 cm (dia.) x 1.8 m]

SPIKED RESERVOIR (1800 liter cap.)

CONTROL RESERVOIR (1800 liter cap.)

Interm. siphon bottle

Inflow to water bath

Sample collection sites

Figure III-4

Figure III-5

REACTOR DETAIL

Clear plexiglass cylinder
29.3 cm (dia.) x 1.8 m
(open-ended top)

Entry port
Exit port
Water bath level

Marsh sediment with
emergent grasses

Heavy-duty rubber sheet
secured by hose clamp

connected to an intermediate 16-liter siphon bottle so that the flow rate into each reactor could be regulated. Reactors 1, 2 and 6 received marsh water which had been artificially spiked with ammonium chloride and potassium phosphate (monobasic) to provide levels of 5 mg NH_3-N/l and 2 mg PO_4-P/l in excess of the marsh water content. Reactors 3, 4 and 5 received unmodified marsh water.

Measurements of dissolved oxygen, temperature, pH, and flow rates were taken over a ten day period at 0800 and at 1630 hours in the reactors and boxes. Flow rates during this period were adjusted to a residence time of 2-3 hours. Water samples were taken about two hours prior to these measurements to ensure a proper diel pattern. Sampling commencing at 0600 hours terminated about sunrise, a period of predominate respiration. The afternoon sampling covered a period of considerable photosynthetic activity. Water samples were analyzed for organic nitrogen, ammonia, nitrate, nitrite, total phosphate, orthophosphate, TOC, TSS, and VSS.

CHAPTER IV

RESULTS

INTRODUCTION

The results obtained from the field investigations in the Swan Lake
marsh in upper Lavaca Bay and from the laboratory studies are presented below.
It should be noted that some results for the slurry tests, a minor portion of
the total data collected, are not presented because of the delay in receiving
the results of nutrient laboratory analyses. These will be presented in a
subsequent report, however.

FIELD INVESTIGATIONS

Early in June a one-day aerial survey was made of the study area by
helicopter to locate suitable areas for the field studies in the Lavaca Bay
system. A bayou with associated marshes was noted on the southwest
shore of Swan Lake in upper Lavaca Bay, and this area was eventually chosen
as the study site. It was evident too during the aerial survey that water
levels were very high throughout the area because of recent high rainfalls in
drainage basins for the area.

Three field investigations were conducted at two week intervals during
the summer to define the hydrologic and water quality characteristics of
the selected marsh area. The first two sampling runs lasted for 24 hours
each (June 27-28, July 11-12), while the third trip covered 48 hours (July 30-
August 1). Normal semi-diurnal tides persisted during the shorter trips, but
a diurnal tidal regime during the final field trip required twice the time to
complete a single tide cycle.

Field Trip on June 27-28, 1974

Field and Weather Conditions

Although the water level had dropped considerably since the initial
aerial survey of the study area, the marsh area was still extensively inundated.
The bases of saltmarsh bulrush clumps (Scirpus maritimus) were partially
submerged during both flood and ebb tides. Weather conditions during this
first field trip included clear skies, air temperatures between $20^{\circ}C$ and
$29.5^{\circ}C$, and a slight easterly breeze that never surpassed 10 mph. Water

temperatures were slightly higher than air temperatures, reaching a maximum of 31.7°C and dropping as low as 23.2°C.

Hydrologic Conditions

Monitoring of the various hydrologic (water depth and velocity) and water quality parameters began during ebb slack and proceeded through one and one-half tidal cycles. The changes in magnitude and direction of water velocities measured at Stations 1, 2, and 3 responded to tidal level changes (see Figure IV-1). Maximum ebb and flood velocities in the main bayou (at Station 1) released 0.7 fps; velocities at other stations were roughly half that amount.

Water particle movement through the major bayou (Station 1) showed (in Figure IV-1) that the distance traveled by a water parcel between flood and ebb slacks equaled or exceeded 17,000 feet. This distance far exceeded the actual distance between Swan Lake and the fartherest reaches of the marsh (over 2500 ft). Thus, the origin of the water passing through the marsh bayou system was Swan Lake water during the flood periods, whereas the larger ponds and pot-holes in the inundated marsh supplied most of the water during the ebbing flow.

The flows computed at each station for all three field trips are given in Table IV-1. During the tidal cycle under study, water exiting the marsh at Station 1 (10.9 x 10^6 l) more than doubled the quantity entering during the preceding flood period (4.5 x 10^6 l). This pattern also prevailed at the stations on minor tributaries, reflecting the large amount of water draining from the marsh and the non-uniformity of tidal exchange.

Water Quality Conditions

Water temperature and dissolved oxygen levels exhibited a disrupted diurnal pattern that was affected by the direction of flow (see Figure IV-2). Flow changes during the night brought warmer and more highly oxygenated water into the marsh from Swan Lake during the period when oxygen levels normally would have continued downward in response to sediment and biota respiratory demands. At Stations 2 and 3, a considerable decrease in dissolved oxygen during the night demonstrated the high benthic uptake rates along these small intra-marsh channels. Without the infusion of oxygenated water during the floodtide, standing water in these areas may have become toxic. Reliable estimates of production using the single dissolved oxygen diurnal curve procedures are not possible due to the disrupted diurnal patterns.

Figure IV - 1
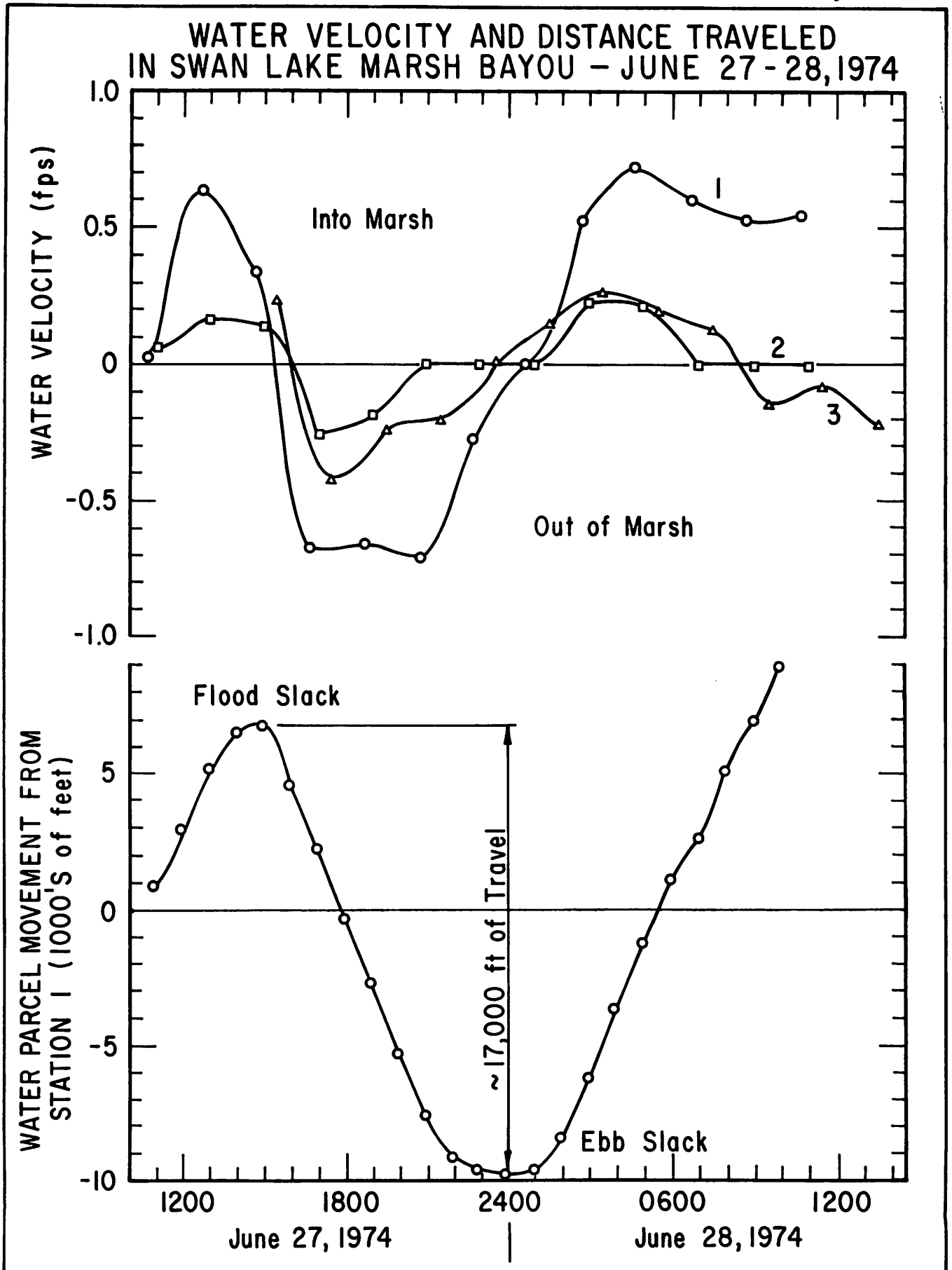
WATER VELOCITY AND DISTANCE TRAVELED
IN SWAN LAKE MARSH BAYOU — JUNE 27-28, 1974
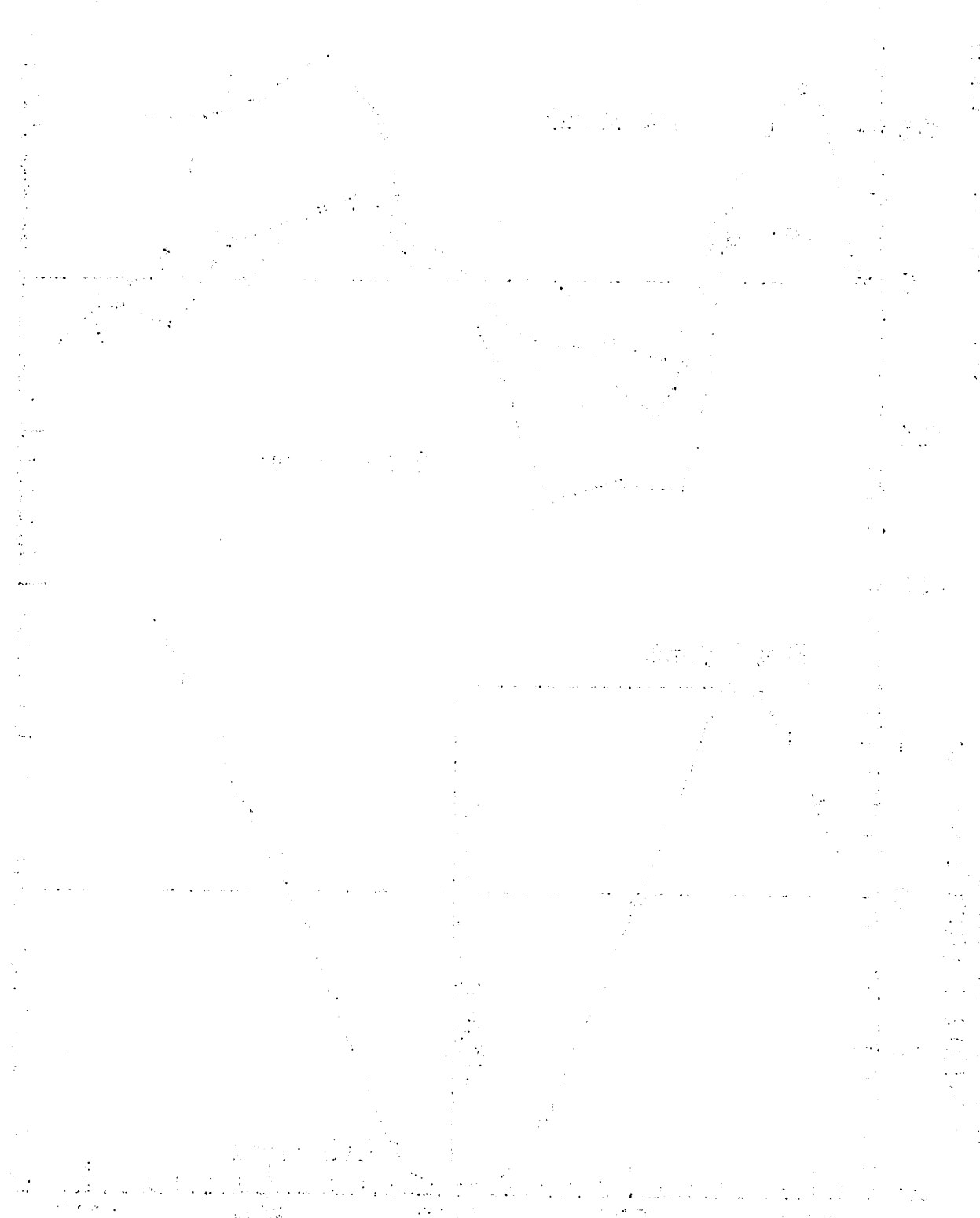
TABLE IV-1

WATER MASS MOVEMENT THROUGH SWAN LAKE MARSH STATIONS
DURING THREE DIFFERENT HYDROLOGIC CONDITIONS

Trip No.	Date	Station	Water movement (liters/tidal cycle)			Comments
			Into Marsh $(10^6 l)$	Out of Marsh $(10^6 l)$	Net Out $(10^6 l)$	
1	June 27-28, 1974	1	4.527	10.886	6.359	Marsh Inundated
		2*	0.066	0.077	0.011	
		3	0.381	0.517	0.136	
		4**	–	–	–	
2	July 11-12, 1974	1	7.386	7.550	0.176	Marsh Partially Inundated
		3	0.454	0.891	0.437	
		4	7.010	5.199	-1.811	
3	July 30-Aug. 1, 1974	1	3.116	4.477	1.361	Marsh Dry
		3	0.749	0.419	-0.330	
		4	2.269	3.354	1.085	

*Station discontinued after first field trip.
**Station not established until second field trip

Figure IV-2

WATER TEMPERATURE AND DISSOLVED OXYGEN CHANGES IN SWAN LAKE MARSH JUNE 27-28, 1974
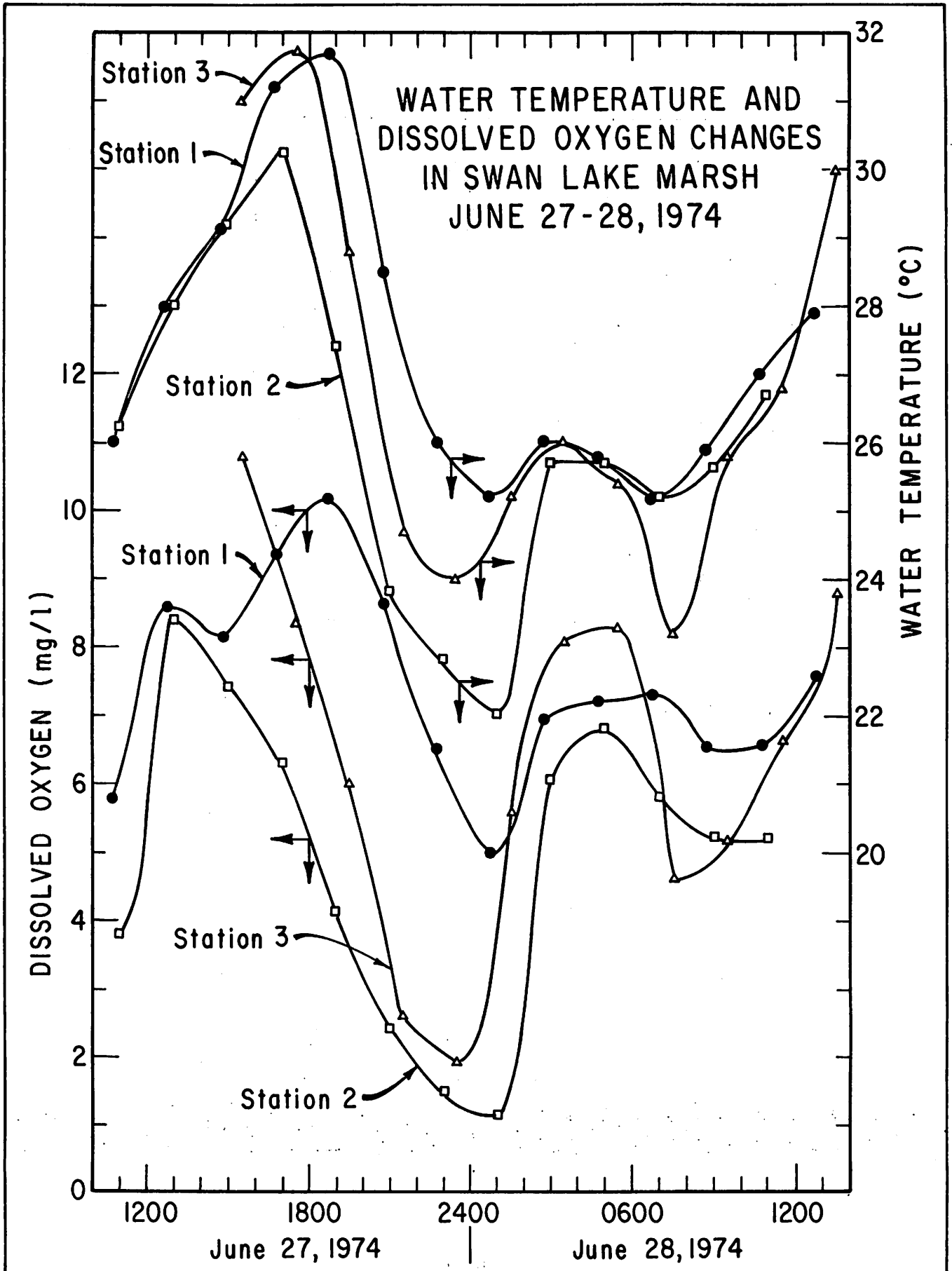
Total organic carbon and organic nitrogen measurements showed slight increases in ambient concentrations during the later stages of outward flow (Figure IV-3). Ammonia levels increased significantly during ebb flow, as would be expected, during washout of this decomposition product while nitrite and nitrate levels remained at the minimum detectable level throughout the sampling period (Figure IV-3). Phosphorus, in both total and soluble forms, exhibited variable concentrations that cannot be correlated directly to specific hydrologic change, although maximum levels were reached at the later stages of ebb flow (Figure IV-4).

Mass flux tabulations for all carbon, nitrogen, and phosphorus nutrient species are given in Table IV-2 and show that more nutrients left the marsh during ebb flow than entered during the preceding flood period. However, this imbalance may be due primarily to the larger volume of water exported during the ebb period, rather than any significantly higher concentrations in marsh outflow waters. As noted above, such higher concentrations were not always evident. The exit of organic nitrogen amounted to three times the inflow quantity, and this magnitude of exchange far exceeded any other nutrient species under study.

Field Trip On July 11-12, 1974

Field and Weather Conditions

During this sampling period, it was found that water levels had receded from the high levels found in June. The marsh vegetation was only partially submerged during the flooding period, but emergent (dry) during the final stages of ebb flow. Clear weather was prevalent on July 11, but early morning cloudiness produced a short but heavy rainstorm at 9 a.m. near the end of sampling on July 12. Air temperatures ranged from 24.1 to 29.3°C, while water temperatures fluctuated between 23.1 and 31.8°C. Winds from the southeast blew at 15-20 mph during the day (July 11), but fell off after sunset and were very light during the early morning hours (0-5 mph) of July 12.

Hydrologic Conditions

Sampling began near the start of a flooding tide, proceeded through one normal tide cycle (15 hours), and then passed through one abbreviated cycle (7 hours) where flow magnitude was much less. Water velocities measured at Stations 1, 3, and 4 (Station 2 was discontinued) are given in Figure IV-5. Like the June data, maximum velocities reached 0.7 fps.

Figure IV-3

TOTAL ORGANIC CARBON AND NITROGEN CHANGES IN SWAN LAKE MARSH − JUNE 27−28,1974

Figure IV-4
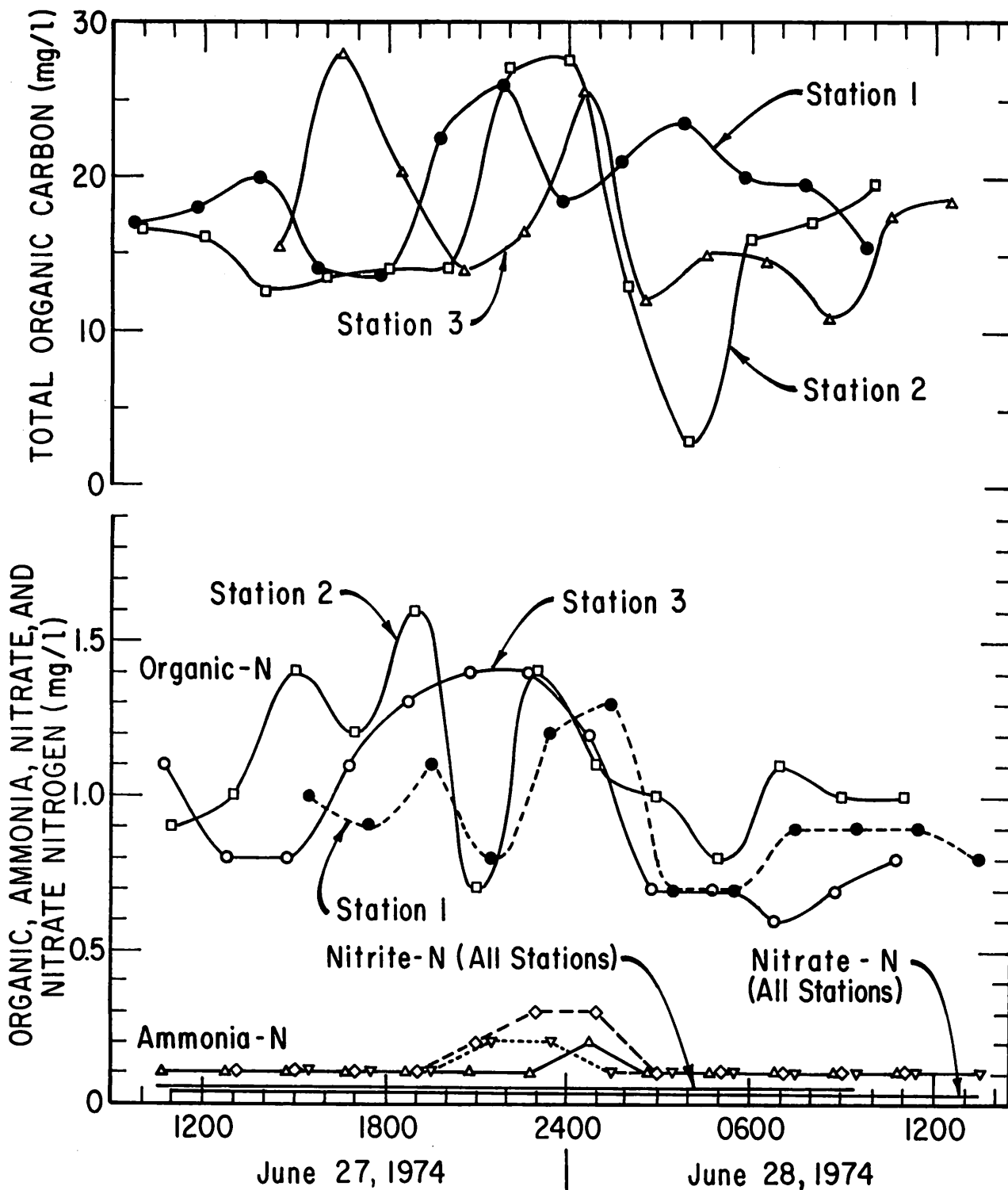
PHOSPHORUS CHANGES IN
SWAN LAKE MARSH BAYOU — JUNE 27-28, 1974
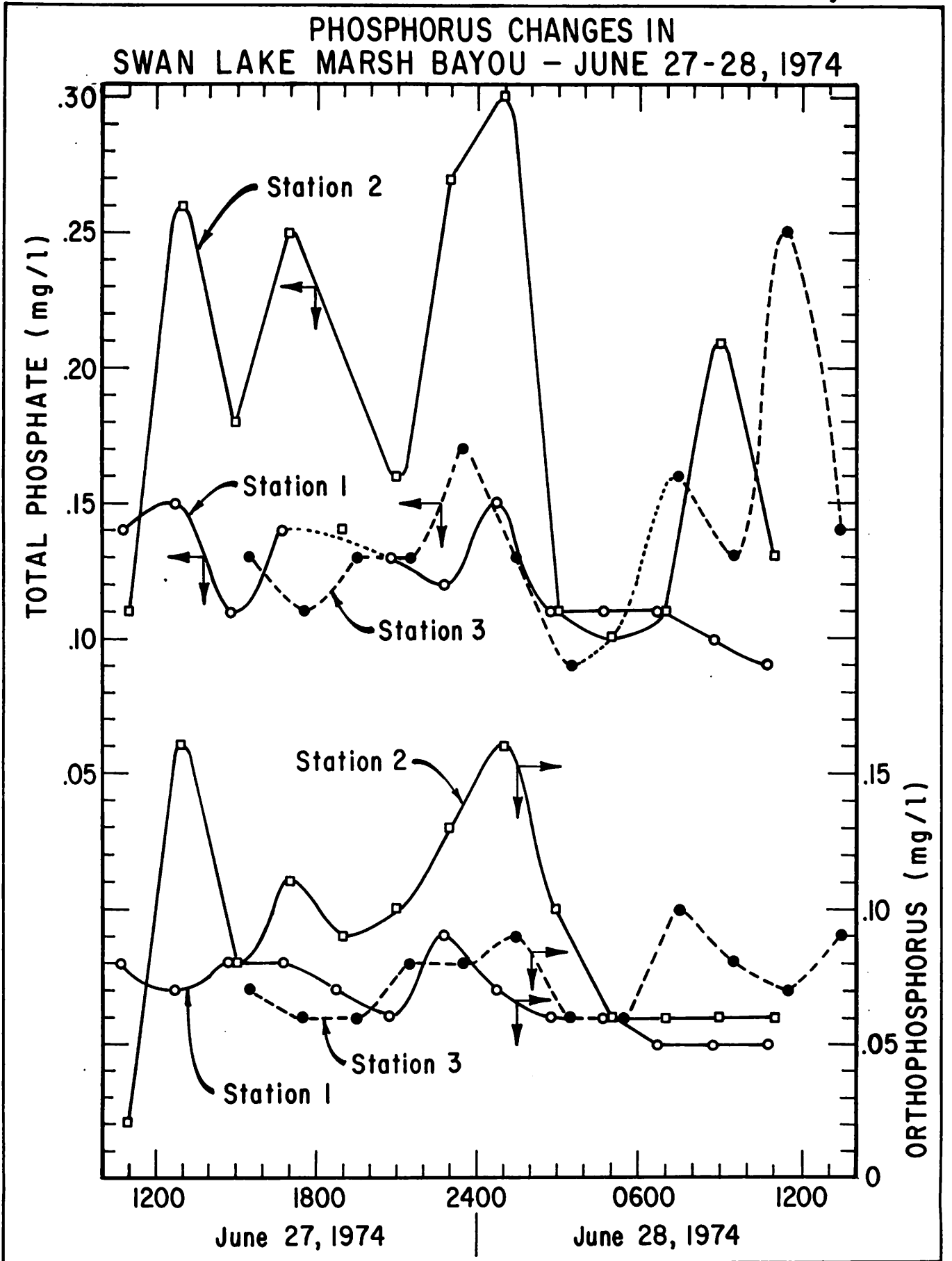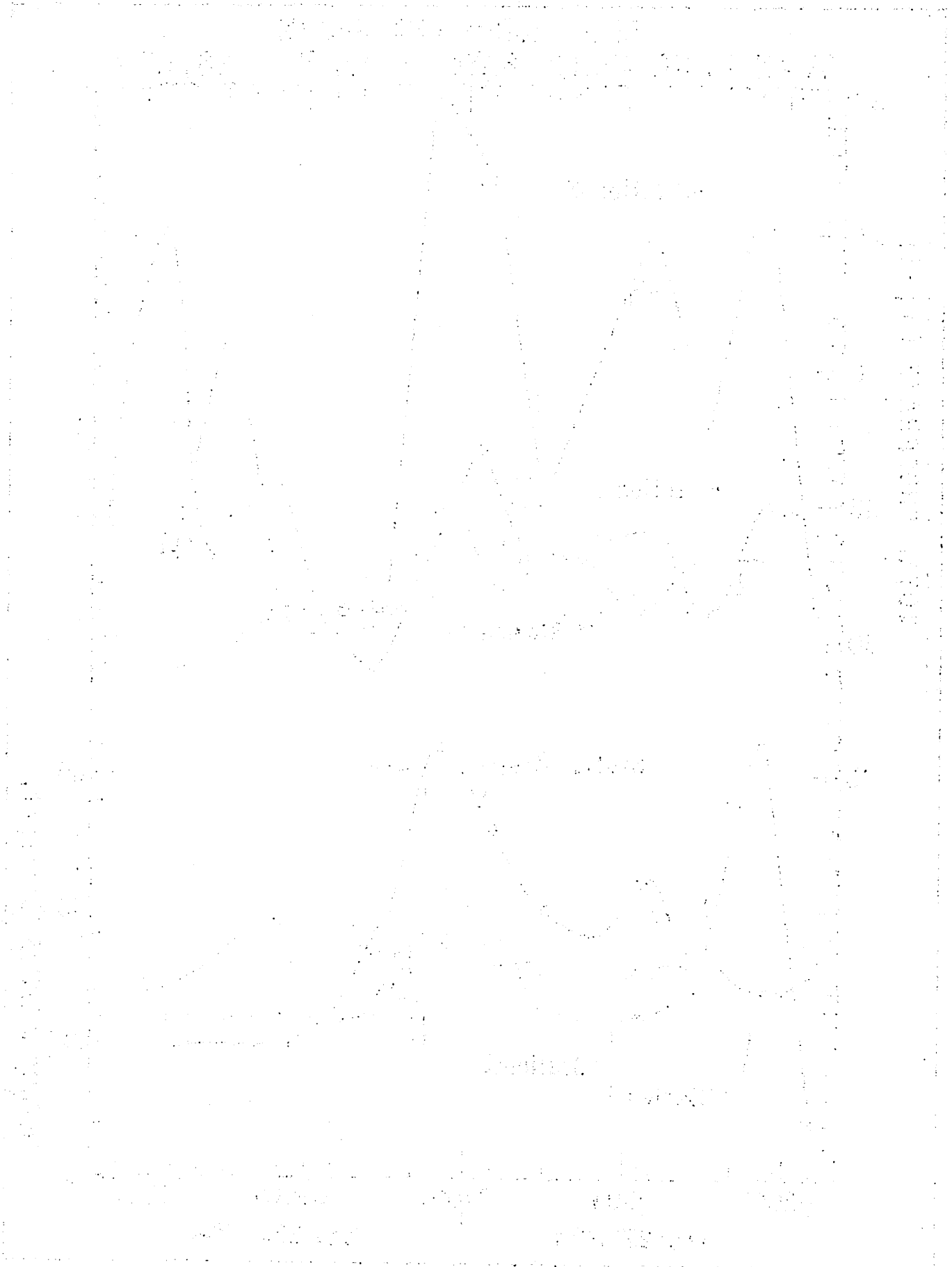
TABLE IV-2

MOVEMENT OF CARBON, NITROGEN, AND PHOSPHORUS AT SWAN LAKE MARSH STATIONS - FIRST FIELD TRIP (June 27-28, 1974)

Station	Nutrient Flows (g/tidal cycle)	Carbon		Nitrogen				Phosphorus	
		TOC	VSS	Org N	NH_3	NO_2**	NO_3**	Total	Ortho
1	Mass In	82,650	*	3,255	436	225	133	648	333
	Mass Out	194,750	*	14,215	1,092	558	299	1,543	826
	Net Mass Flow Out	112,100	*	10,960	656	333	166	895	493
2	Mass In	985	*	85	8.3	3.4	2.1	14.7	8.20
	Mass Out	1,248	*	121	8.7	4.3	2.6	17.7	8.26
	Net Mass Flow Out	263	*	36	0.4	0.9	0.5	3	0.06
3	Mass In	5,540	*	1,045	40	33	14.2	46	30
	Mass Out	9,340	*	1,130	80	21	16.4	83	43
	Net Mass Flow Out	3,800	*	85	40	- 12	2.2	37	13

*No measurements taken
**Based on minimum detectable levels

The maximum distance traveled by a water particle upstream or down-stream (10,000 ft) was somewhat less than for the first field trip (Figure IV-5), but was still far enough to indicate complete movement of water from Swan Lake into the interior marsh.

It is noted in Table IV-1 that water exchange through Station 1 in the main bayou channel was essentially equal for both phases of the normal tide cycle. Other sampling sites exhibited different patterns of water movement. Station 3 in the tributary bayou discharged twice as much water to the main bayou on the ebb tide as it received from the bayou on the flood tide, indicating that water movemement from Swan Lake to the drainage arch of this small tributary may be a major exchange route at this water level. However, the back marsh bayou channel (Station 4) received more water on the flooding tide than it released on the ebb tide. High evaporation and transpiration rates on this hot, windy day may have been responsible for most of the water loss observed.

Water Quality Conditions

Diurnal water temperature and dissolved oxygen patterns were much more "normal" than during the first sampling trip (see Figure IV-6), but the incoming water did alter the magnitude of change slightly. The diurnal pattern was stable enough to calculate a daily gross production rate of 12.8 g/m^3/day for Station 1 on the main bayou channel. For the average depth of 2.6 ft, the areal gross production rate is 10.2 g/m^2/day. Since the total respiration rate was the same, the P/R ratio equaled one. However, these productivity estimates result only from benthic algae and phytoplankton activity, rather than rooted vegetation.

Carbon, measured as TOC and VSS, remained relatively stable throughout the entire 24 hours period for all stations as can be seen in Figure IV-7, except for several excessive VSS peaks at Station 4. These peaks in VSS seemed to occur during changes in direction of water flow when thick surface films became most apparent. TOC levels tended to decrease during flood tide and increase during ebb tide, but remained between 8 and 24 mg/l.

Ambient concentrations of ammonia and organic nitrogen peaked at the end of marsh outflow, but levels of nitrite and nitrate remained constant regardless of the direction of water movement (Figure IV-8). Total phosphorus and orthophosphorus persisted at low levels (less than 0.17 mg/l) throughout the entire sampling period (Figure IV-8).

Figure IV-5

WATER VELOCITY AND DISTANCE TRAVELED IN SWAN LAKE MARSH BAYOU — JULY 11-12, 1974
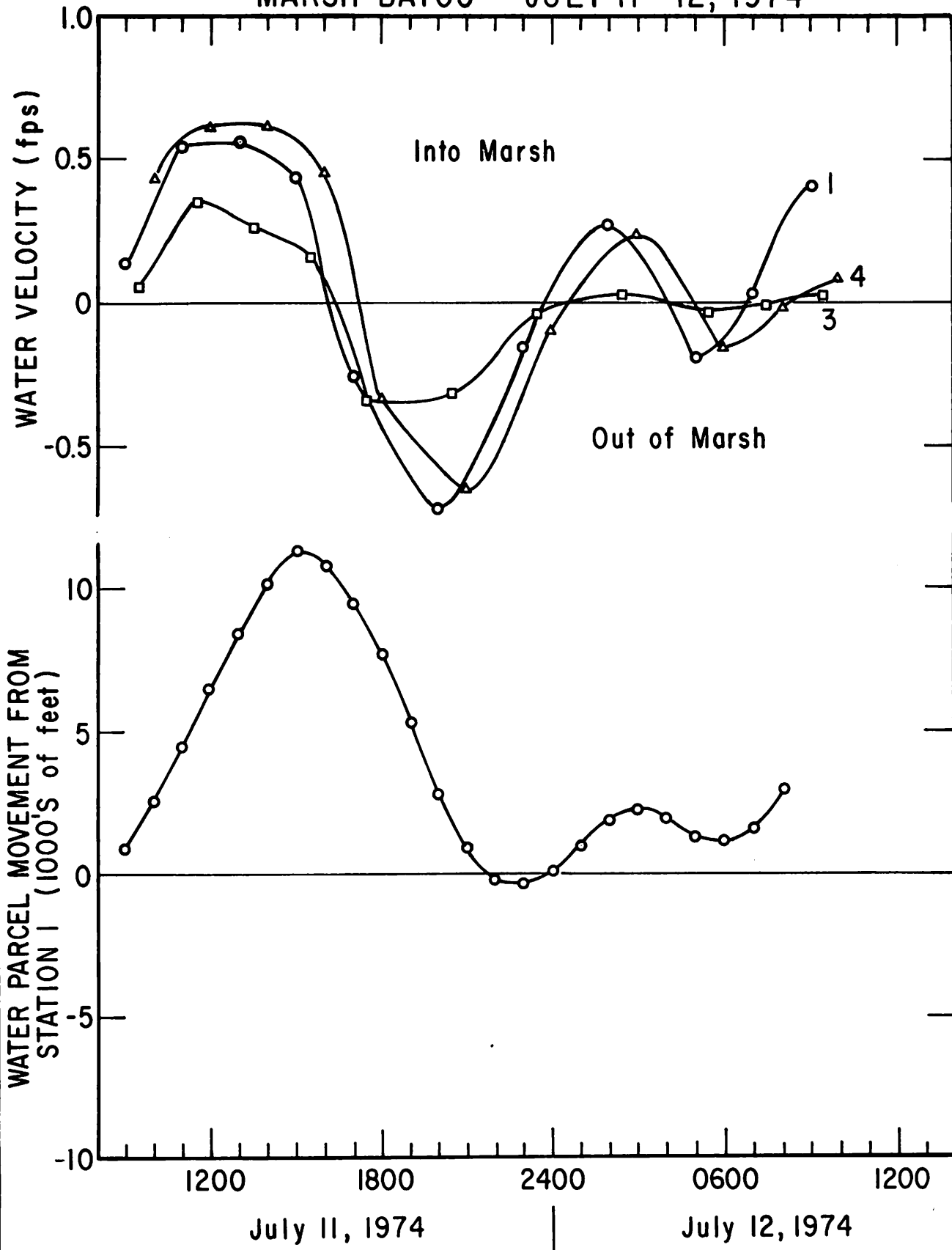
Figure IV-6

WATER TEMPERATURE AND DISSOLVED OXYGEN CHANGES IN SWAN LAKE MARSH BAYOU — JULY 11-12, 1974

Figure IV- 7

ORGANIC CARBON CHANGES IN
SWAN LAKE MARSH BAYOU – JULY 11-12,1974

Figure IV-8
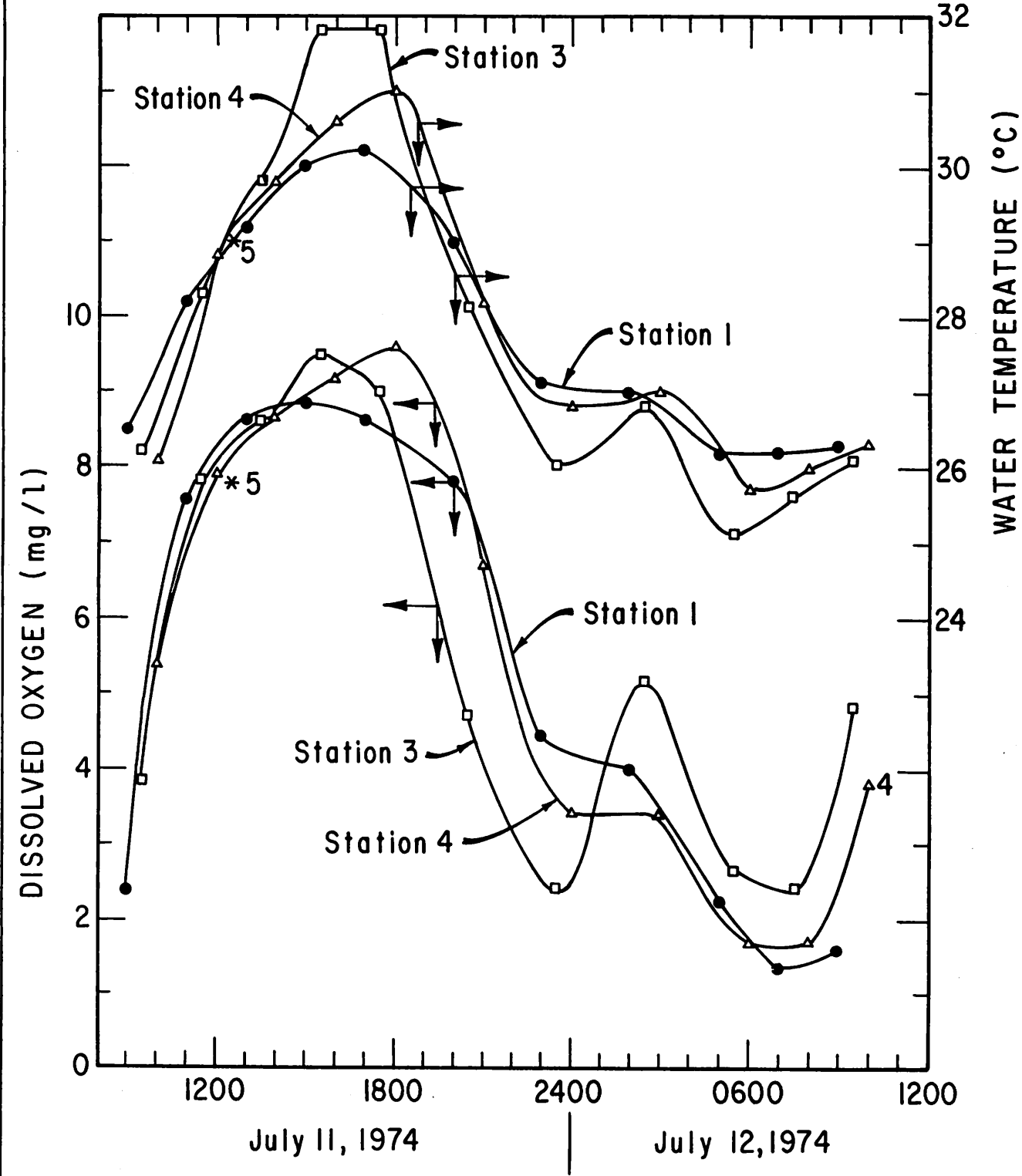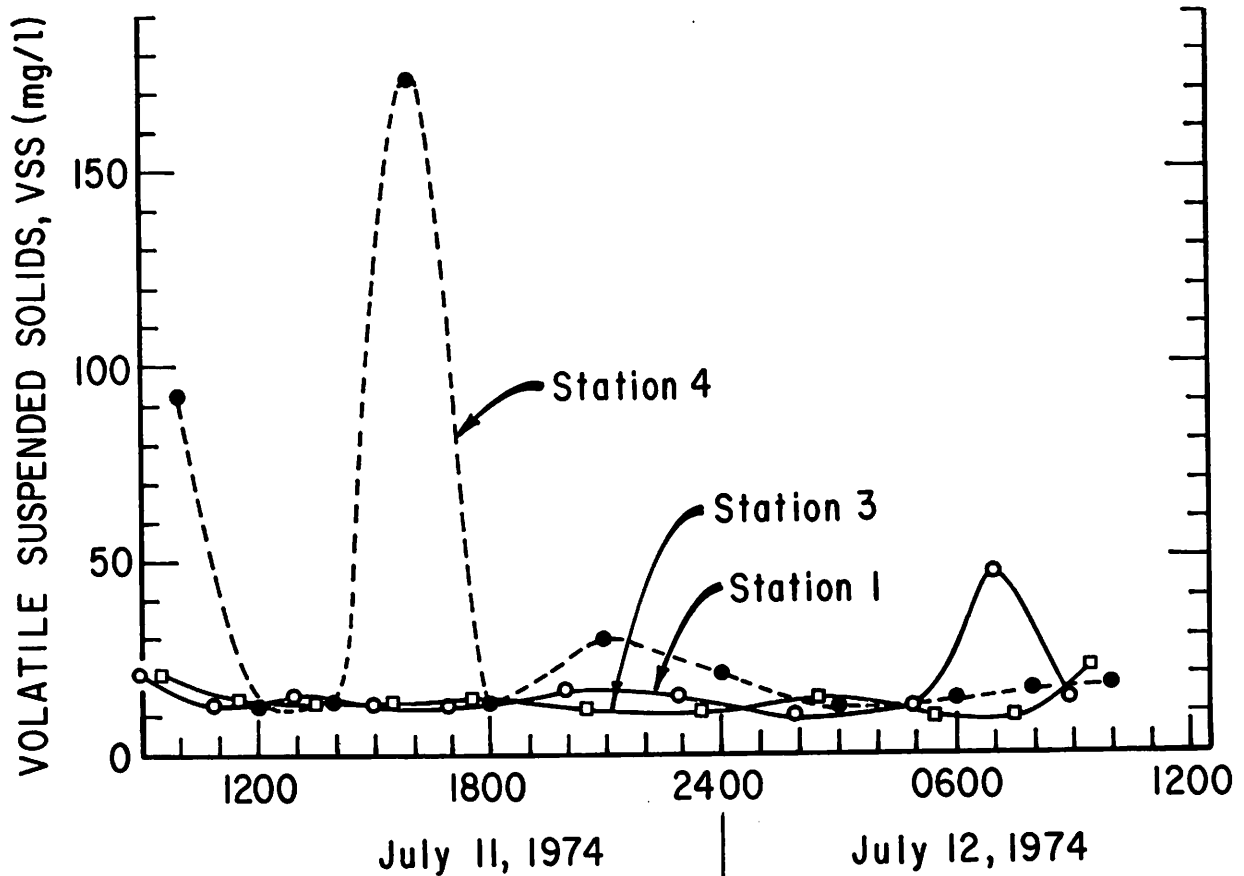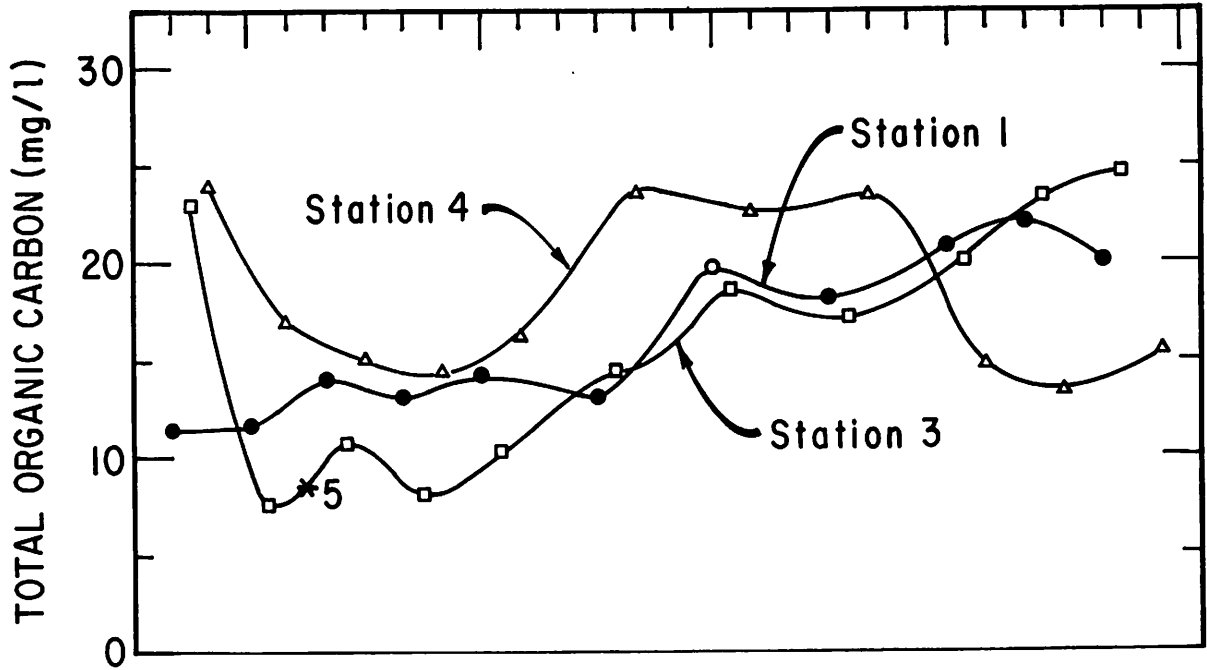
NITROGEN AND PHOSPHORUS CHANGES IN
SWAN LAKE MARSH BAYOU — JULY 11-12, 1974
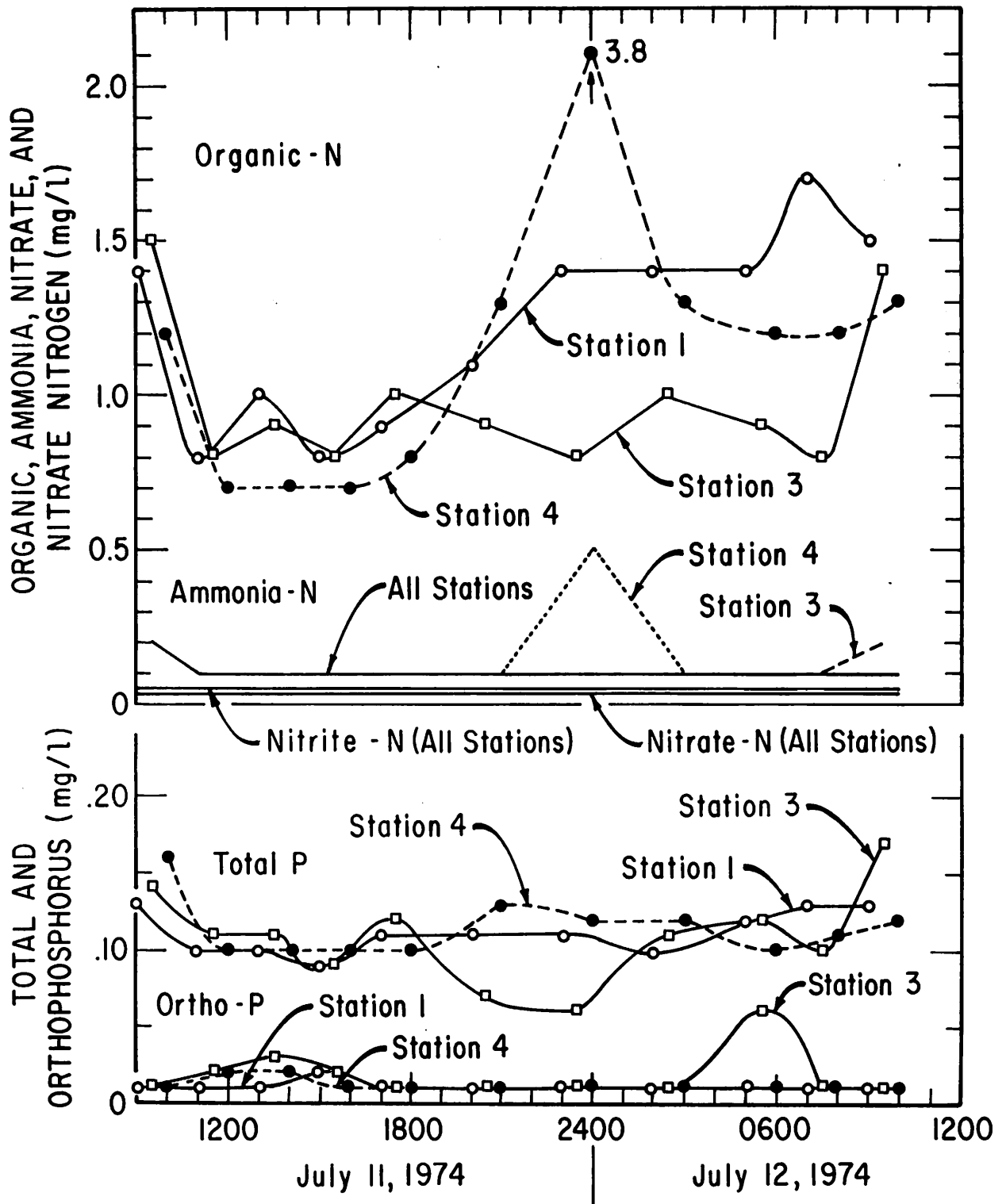
Mass flux data (Table IV-3) showed that organic nutrients (TOC, VSS, organic nitrogen) showed greater outflows from the marsh during the tidal cycle. Inorganic nutrients (NH_3, NO_2, NO_3) needed for algal and vascular plant growth exhibited a slight loss to the marsh. Orthophosphorus exhibited a distinct loss to the marsh, as did total phosphorus in the back region of the marsh. However, a small net transport out of the marsh for total phosphorus was observed through Station 1.

Field Trip On July 30-August 1, 1974

Field and Weather Conditions

This final field trip (48 hours duration) was originally conceived to delineate the water and nutrient mass flows over several tidal cycles instead of only one cycle as the previous two field trips had been. However, in the interim period the tidal regime had changed from semi-diurnal to diurnal, so the same number of tidal cycles was investigated. Water levels had dropped below levels recorded during previous trips, and the bayou channels almost emptied completely during ebb tide in this sampling period. The marsh was almost dry, with the water mainly confined to the marsh channels and larger pot-holes during both blood and ebb periods. Marsh vegetation was almost exclusively emergent. The weather during this 48-hour trip varied considerably from clear skies to imposing thunderhead formations. However, only a slight drizzle fell to break the chronic summertime drought during the second day. Air temperatures reached a maximum of $32.8^{\circ}C$ during the late afternoon, and this contributed to raising the bayou water temperature as high as $34.9^{\circ}C$. Winds were generally calm (slight breezes from the north) during periods of precipitation, but, as skies cleared, they switched to the southeast with a velocity of 10-15 mph.

Hydrologic Conditions

Water movement was restricted exclusively to the bayou channel, larger tributaries, and contiguous pot-holes between Swan Lake and the interior bi-lobed pond system. Water velocities were generally lower in the main bayou than on previous field trips, and a trend toward net movement into the marsh is evident from the velocity data plotted in Figure IV-9. Even though the time of directional flow was increased under the prevailing tidal regime, the volume of water exchanged was much smaller (roughly one-half) than that observed on earlier field trips (Table IV-1). Also, the distance

TABLE IV-3

MOVEMENT OF CARBON, NITROGEN, AND PHOSPHORUS AT SWAN LAKE MARSH STATIONS – SECOND FIELD TRIP (July 11-12, 1974)

Station	Nutrient Flows (g/tidal cycle)	Carbon		Nitrogen				Phosphorus	
		TOC	VSS	Org N	NH_3	NO_2*	NO_3*	Total	Ortho
1	Mass In	97,600	99,450	6,800	771	366	226	742	100
	Mass Out	104,750	111,100	8,390	748	384	231	802	75
	Net Mass Flow Out	7,150	11,650	1,590	- 23	18	5	60	- 25
3	Mass In	4,340	6,370	8,080	49.5	24.5	22.7	48.4	10.7
	Mass Out	7,080	6,220	10,240	54.2	26	26	50.2	5
	Net Mass Flow Out	2,740	- 150	2,160	4.7	1.5	3.3	1.8	-5.7
4	Mass In	142,400	471,500	6,240	964	360	231	837	129
	Mass Out	129,100	153,500	6,420	759	296	147	721	57
	Net Mass Flow Out	-13,300	-318,000	180	-205	- 64	- 84	-116	- 72

*Based on minimum detectable levels

Figure IV-9

WATER VELOCITY AND DISTANCE TRAVELED IN SWAN LAKE MARSH BAYOU – JULY 30 – AUGUST 1, 1974
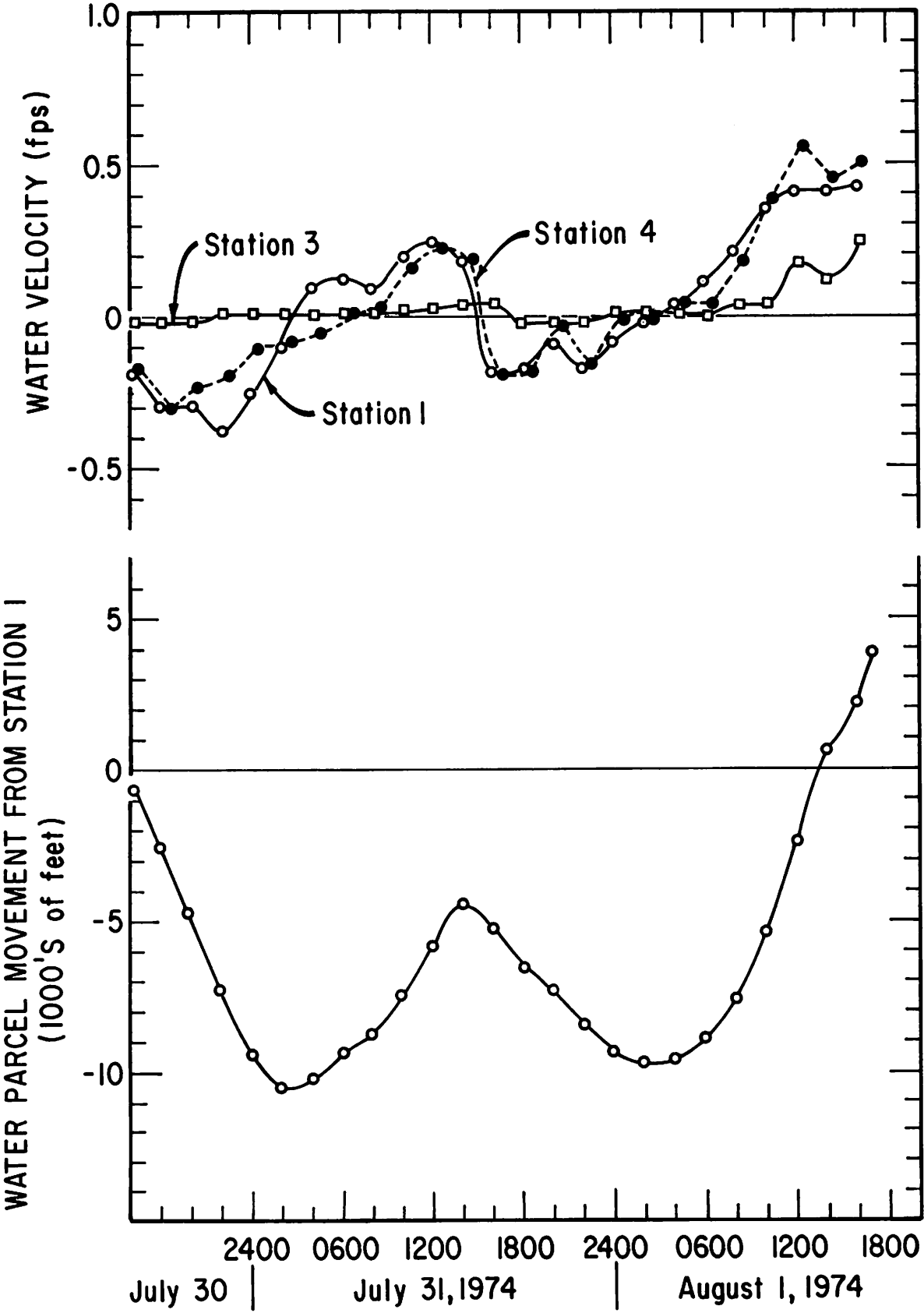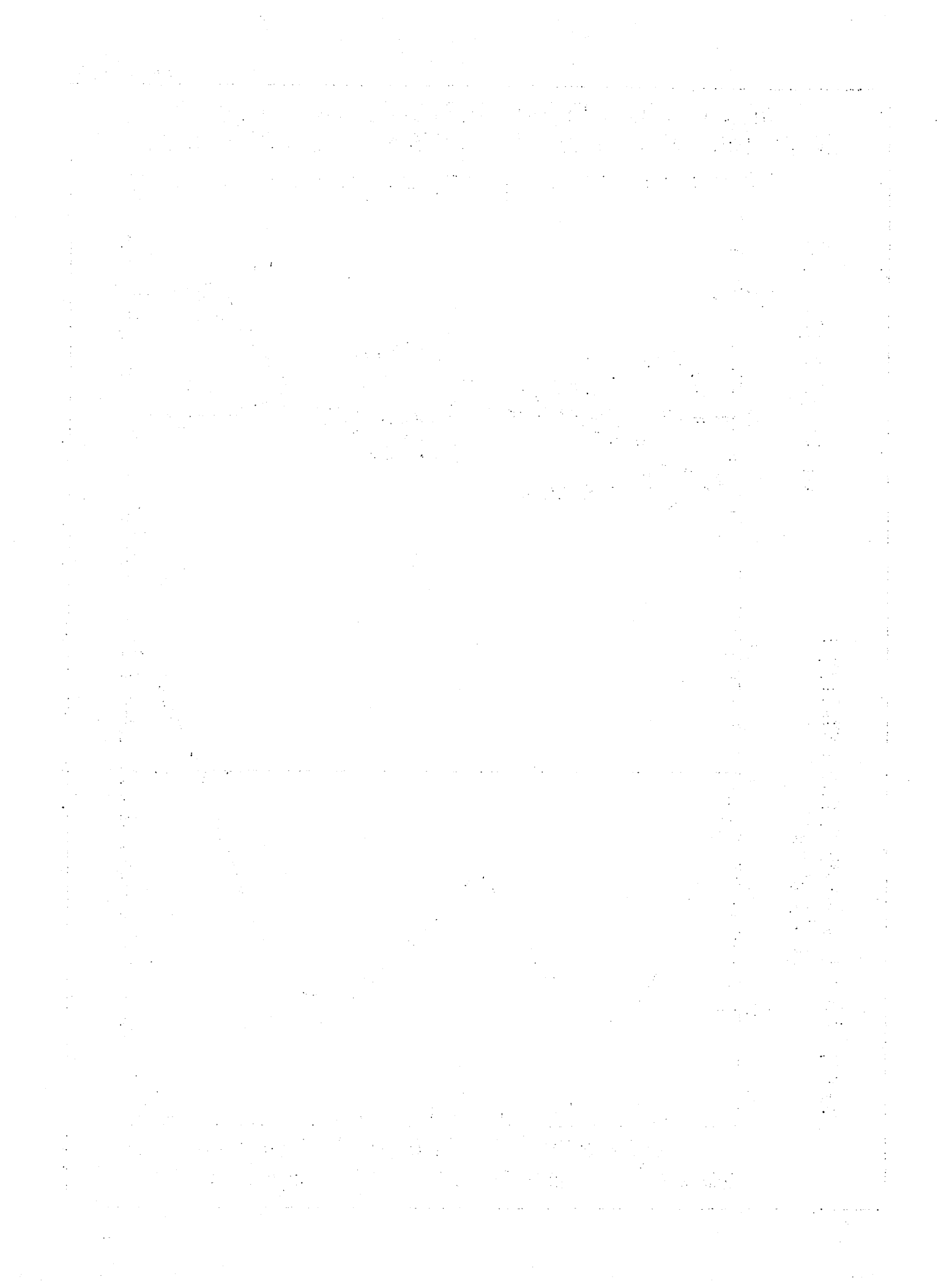
traveled upstream or downstream by a water parcel continued to decrease from previous field trips (see Figure IV-9).

Water Quality Conditions

Temperature and dissolved oxygen fluctuated drastically each day, reaching $34.9^\circ C$ and 10 mg/l during the day and dropping to $24^\circ C$ and near zero mg/l during the early morning hours as the marsh emptied on the ebb tide (see Figures IV-10 and IV-11). Calculated community respiration in the marsh water (Station 1) amounted to 18.6 $g/m^3/day$ gross production (14.7 $g/m^2/day$) and 18.4 $g/m^3/day$ total respiration (14.6 $g/m^2/day$). The combination of low water level and high respiratory demand resulted in anoxic conditions which adversely affected the marsh biota. Fish kills of mullet and various sciaenid fishes occurred during these stressful conditions. Blue crabs adjusted to the oxygen depletion by migrating out of the water as the oxygen level dropped. When rapid photosynthesis and wind-aided reaeration restored a reasonable concentration after sunrise, the crabs moved back into the marsh waters.

TOC and VSS levels greatly exceeded concentrations found in previous trips, as TOC levels reached 60 mg/l (Figure IV-12) and VSS concentrations exceeded 100 mg/l (Figure IV-13). Carbon concentrations varied directly with the direction of flow, increasing significantly as the marsh drained on the ebb tide.

Organic nitrogen concentrations exhibited a similar tide-related pattern, and several values above 4 mg/l surpassed previous maximum concentrations (see Figure IV-14). Ammonia variation closely followed the organic nitrogen pattern and also reached higher concentrations than noted before (Figure IV-14). Nitrite and nitrate remained at minimum detection levels (Figure IV-14). Both orthophosphorus and total phosphorus reached peak levels of 0.32 and 0.72 mg/l respectively (Figure IV-15).

Mass balances for all carbon, nitrogen, and phosphorus species under study showed a larger exodus of material than was transported into the marsh (Table IV-4). This outward transport was greatest for the organic nutrients, but was also considerable for inorganic nitrogen and phosphorus forms.

Figure IV - 10

TEMPERATURE CHANGES
IN SWAN LAKE MARSH BAYOU
JULY 30 - AUGUST 1, 1974

Figure IV – 11
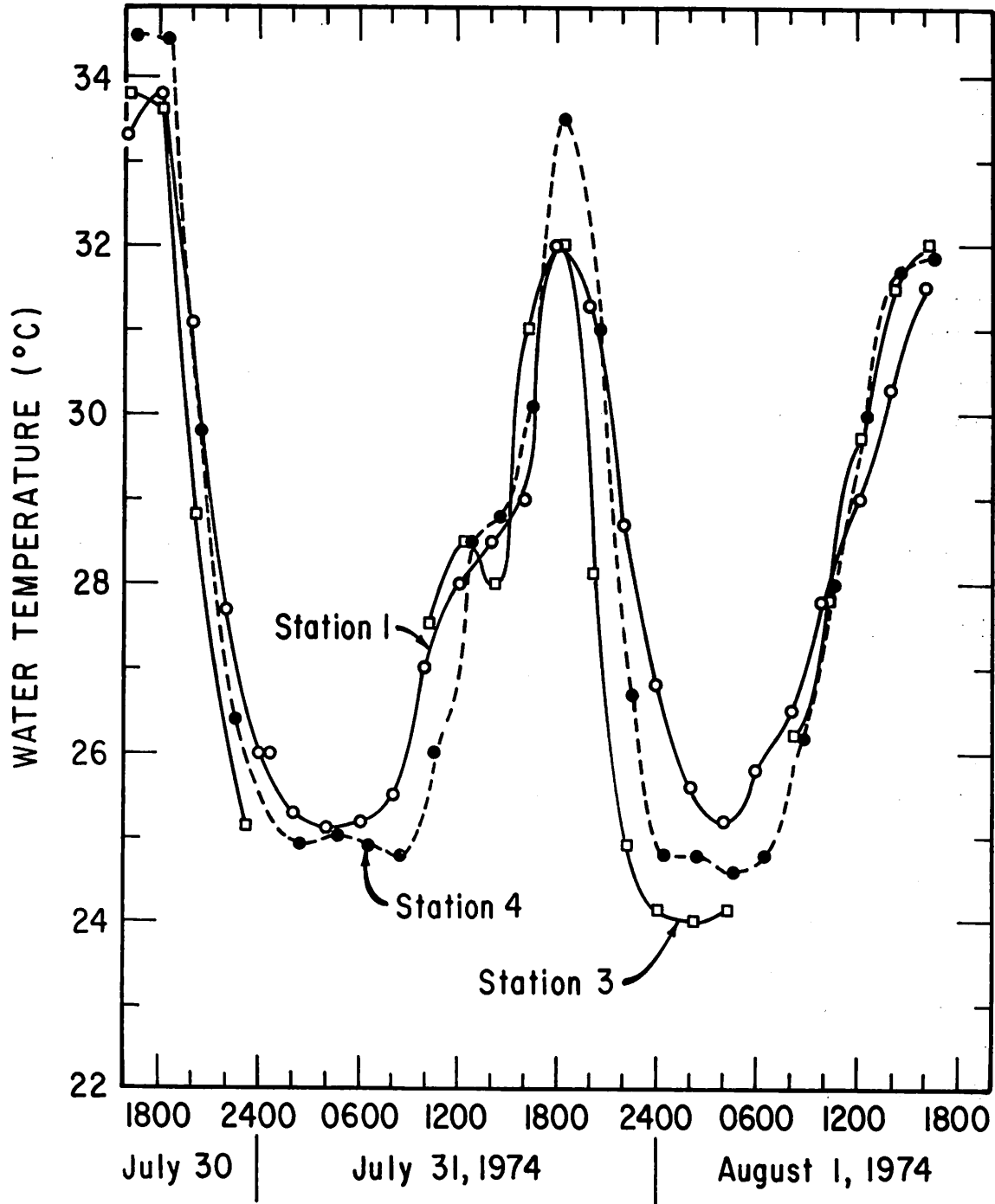
DISSOLVED OXYGEN IN SWAN LAKE MARSH BAYOU
JULY 30 – AUGUST 1, 1974

Figure IV-12
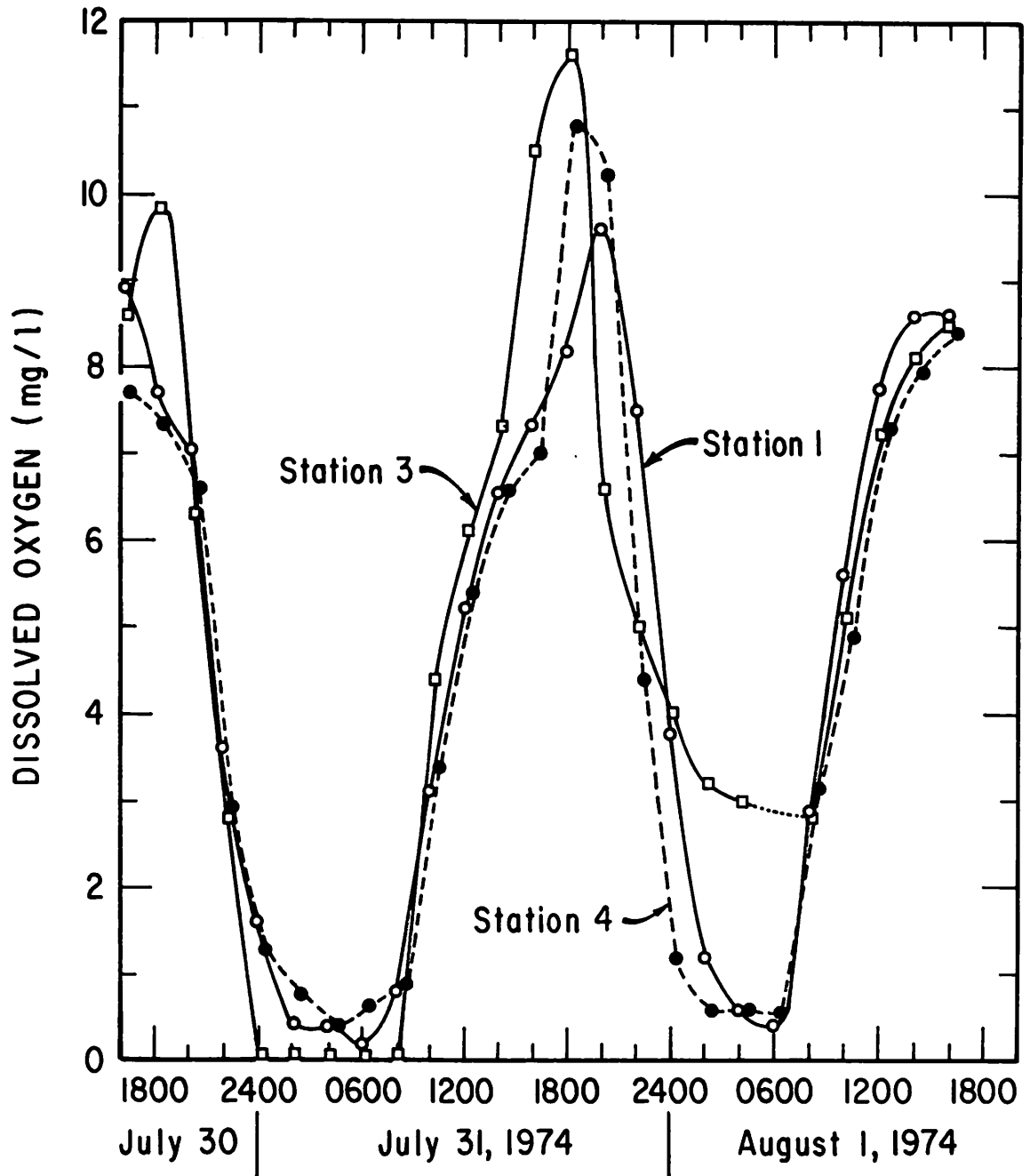
TOTAL ORGANIC CARBON CHANGES IN
SWAN LAKE MARSH BAYOU
JULY 30 – AUGUST 1, 1974

Figure IV-13
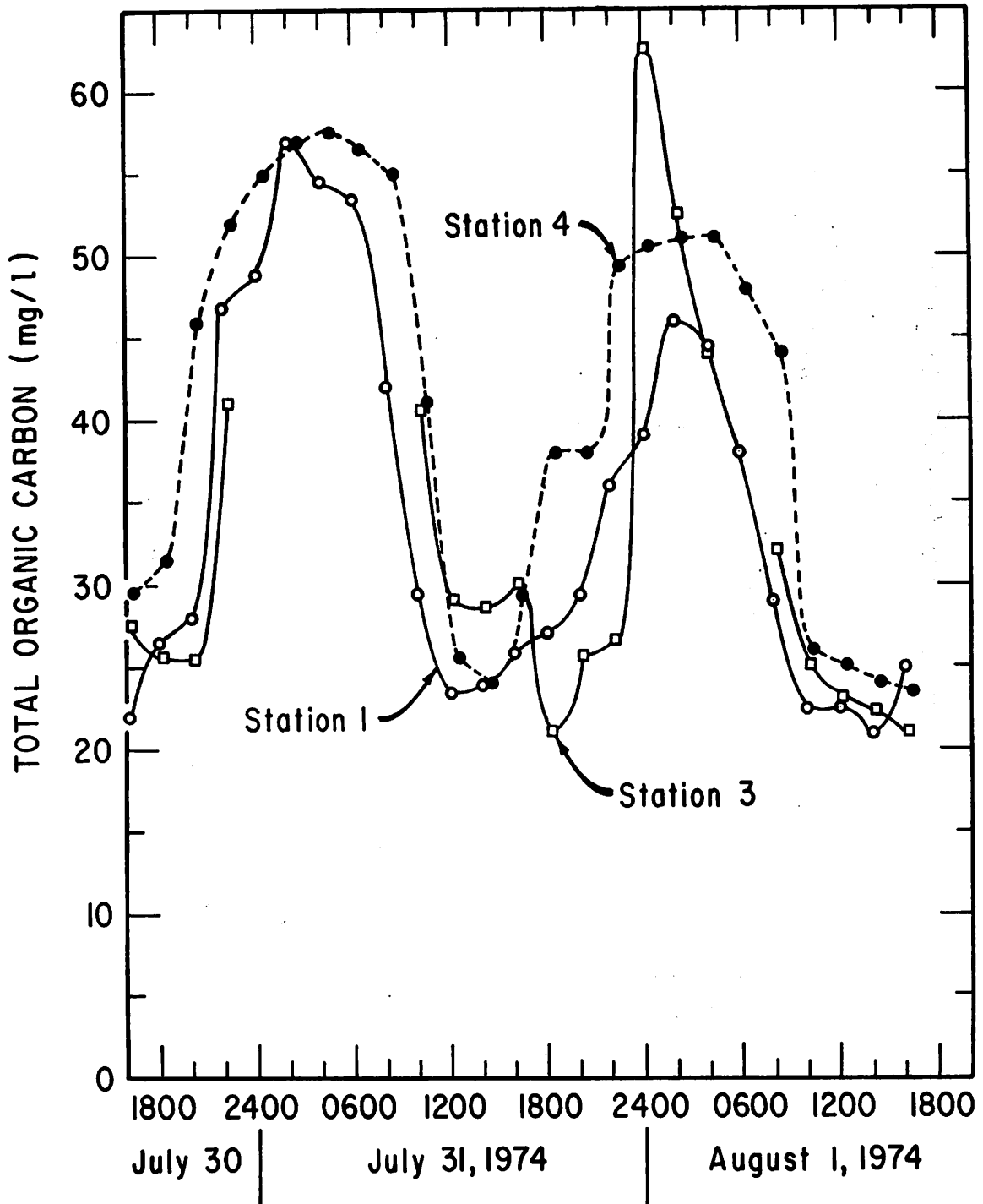
ORGANIC MATERIAL (VOLATILE SUSPENDED SOLIDS)
IN SWAN LAKE MARSH BAYOU
JULY 30 – AUGUST 1, 1974

Figure IV – 14

NITROGEN CHANGES IN SWAN LAKE MARSH JULY 30 – AUG. 1, 1974

Figure IV - 15

TOTAL AND ORTHOPHOSHORUS
CHANGES IN SWAN LAKE
MARSH BAYOU
JULY 30 - AUGUST 1, 1974
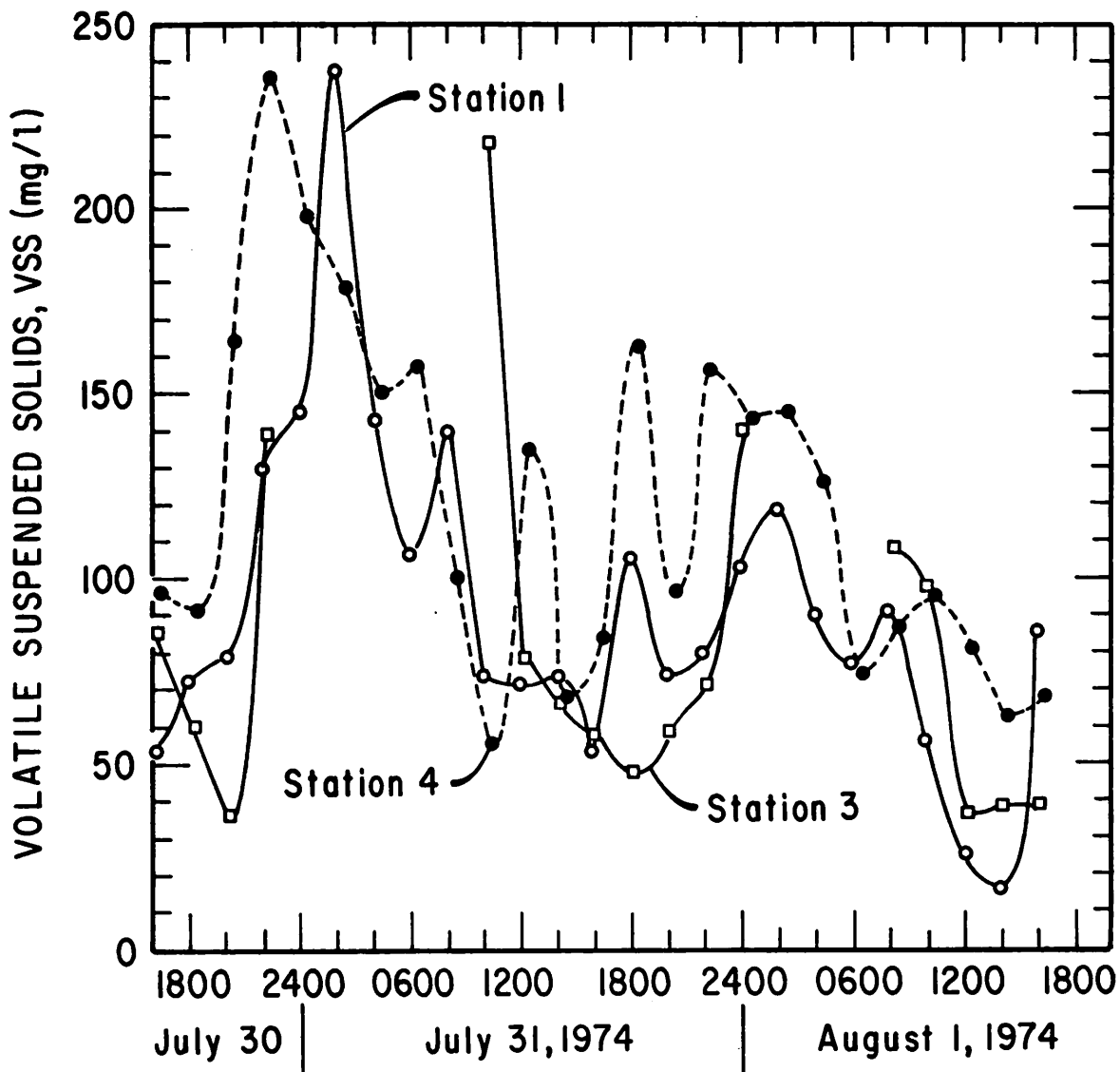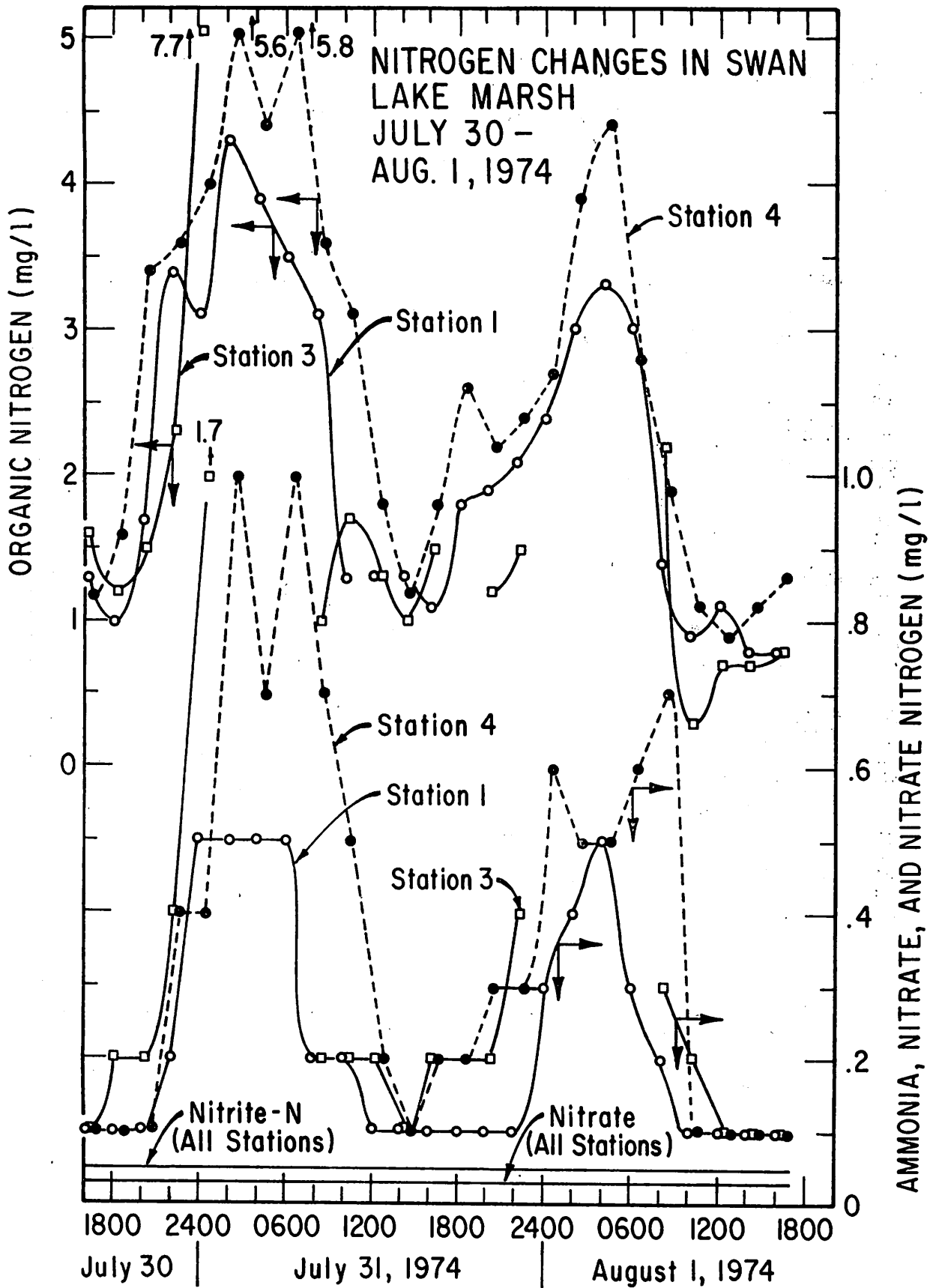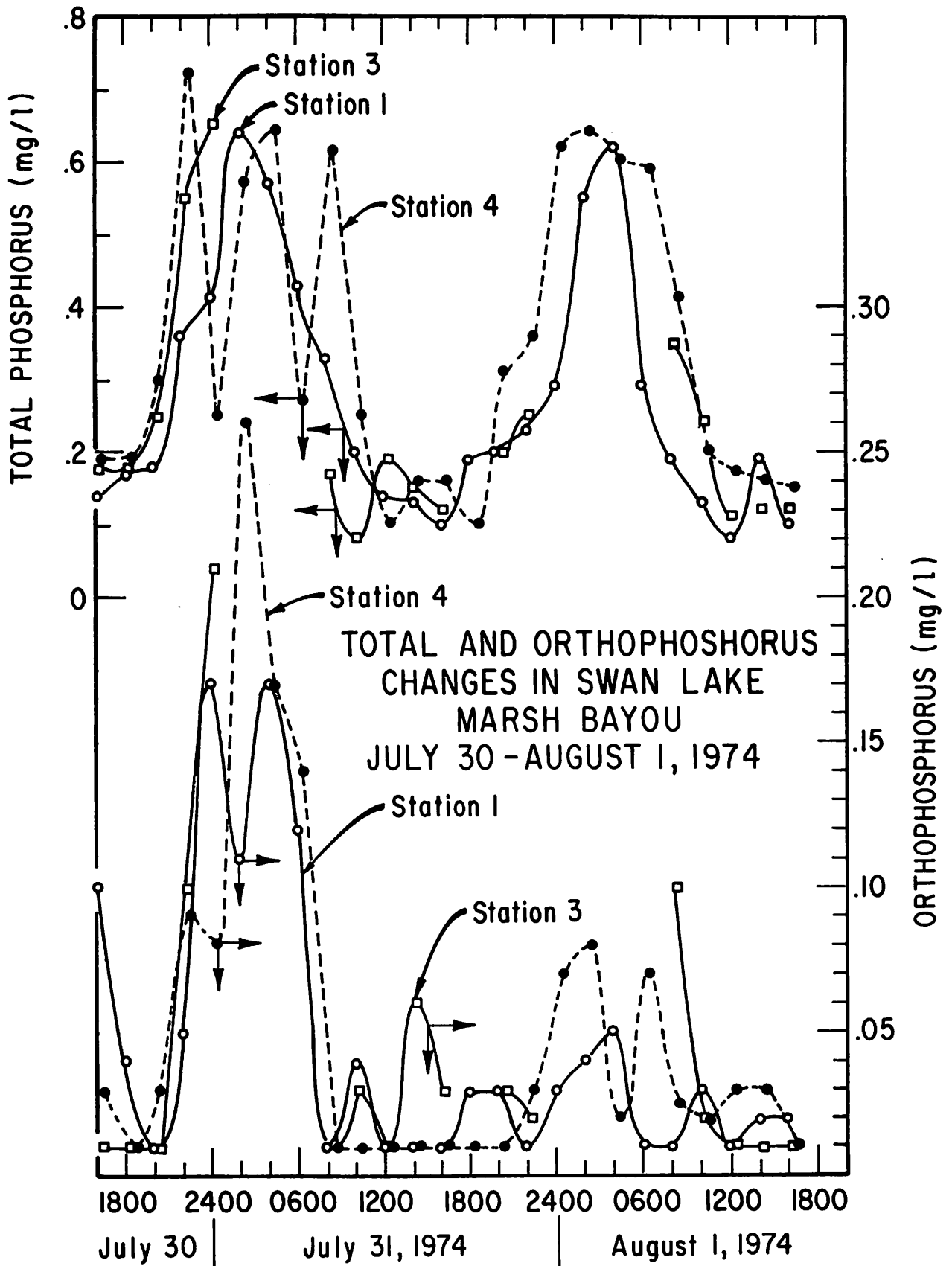
TABLE IV-4
MOVEMENT OF CARBON, NITROGEN, AND PHOSPHORUS AT SWAN LAKE MARSH STATIONS –
THIRD FIELD TRIP (July 30–August 1, 1974)

Station	Nutrient Flows (g/tidal cycle)	Carbon		Nitrogen				Phosphorus	
		TOC	VSS	Org N	NH_3	NO_2*	NO_3*	Total	Ortho
1	Mass In	82,600	222,000	6,540	679	152.9	94	733	136
	Mass Out	152,600	436,000	9,390	831	229.6	136	1,140	329
	Net Mass Flow Out	70,000	214,000	2,850	152	76.7	42	407	193
3	Mass In	720	1,700	341	3.90	1.34	0.67	3.44	0.75
	Mass Out	720	2,740	47.8	3.97	1.43	0.83	5.36	0.35
	Net Mass Flow Out	0	1,040	13.7	0.07	0.09	0.16	1.92	-0.40
4	Mass In	63,100	200,000	4,940	708	103.3	61.5	396	51
	Mass Out	136,300	458,000	7,380	745	165.1	102.6	1,017	185
	Net Mass Flow Out	13,200	258,000	2,440	37	61.8	41.1	621	134

*Based on minimum detectable levels

LABORATORY INVESTIGATIONS

Slurry Tests

As mentioned earlier, the results for the slurry tests will not be presented here because the laboratory analyses of nitrogen and phosphorus were not completed by the Health Department Laboratory in time for inclusion. These results will be included in a subsequent report which will be prepared for the continuing work on the Lavaca Bay marsh reactor studies.

Fixed Bed Results

Leaching and Spiking Results

Analysis of the fixed bed exchange data was confounded because of two principle problems. The unanticipated poor quality and variability in tap water during the experimental period severely affected the quality of the distilled water used during draw and refill procedures. Additional variability in nutrient levels characterizing different batches of INSTANT OCEAN* and subsequent analysis of blanks have presented inconsistent results. An analysis of the data was carried out; however, it presented here only as a description of an approach and to reveal trends which may or may not be realistic.

The presentation of results will be limited to the leaching and uptake of ammonia. Figures IV-16 and IV-17 show concentrations leached from the sediments to the water column through time (leaching period) at three different salinities and three different temperatures respectively. Note that each data point represents the ammonia concentration at the end of a one day leaching period; the concentrations observed leached from the sediment during that time. Also, each data point represents the mean of results from several cores. Similarly, Figures IV-18 and IV-19 show uptake for the same environmental conditions. These data have not been corrected for background concentrations of ammonia or differences in water volumes. In order to correct for water volume differences and to determine the actual mass of the nutrient in the water column after leaching, the following equation is used:

$$C_w \cdot V = M_{NH_3-N} \qquad \text{(IV-1)}$$

where:

C_w = concentration of NH_3 expressed as NH_3-N (mg/l)

V = volume of water removed (liters), and

M = mass of NH_3 removed expressed as NH_3-N (mg).

Figure IV-16

SALINITY EFFECTS ON AMMONIA
LEACHING FROM SEDIMENTS

Figure IV-17

TEMPERATURE EFFECTS ON AMMONIA LEACHING FROM SEDIMENTS
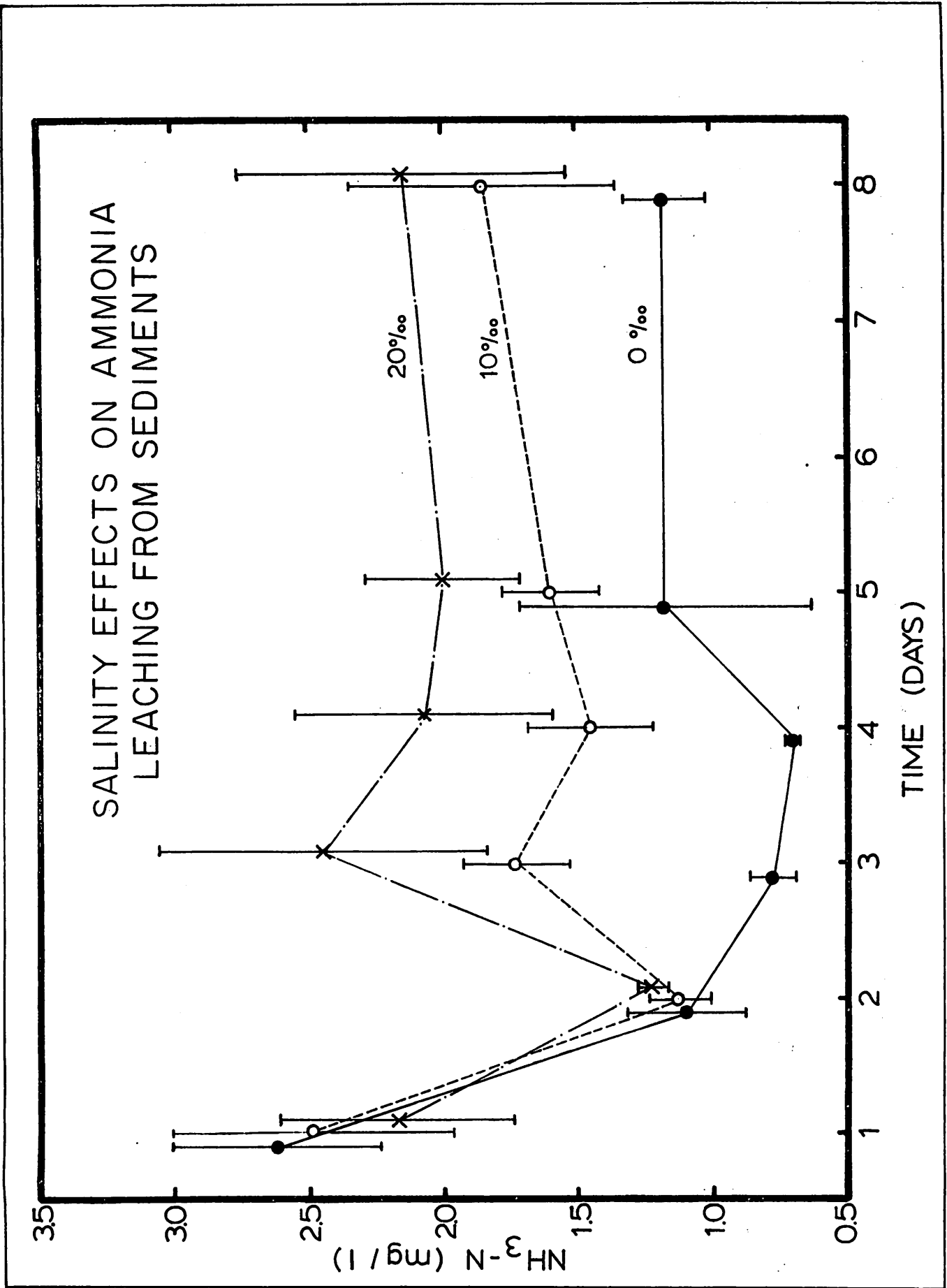
Figure IV – 18
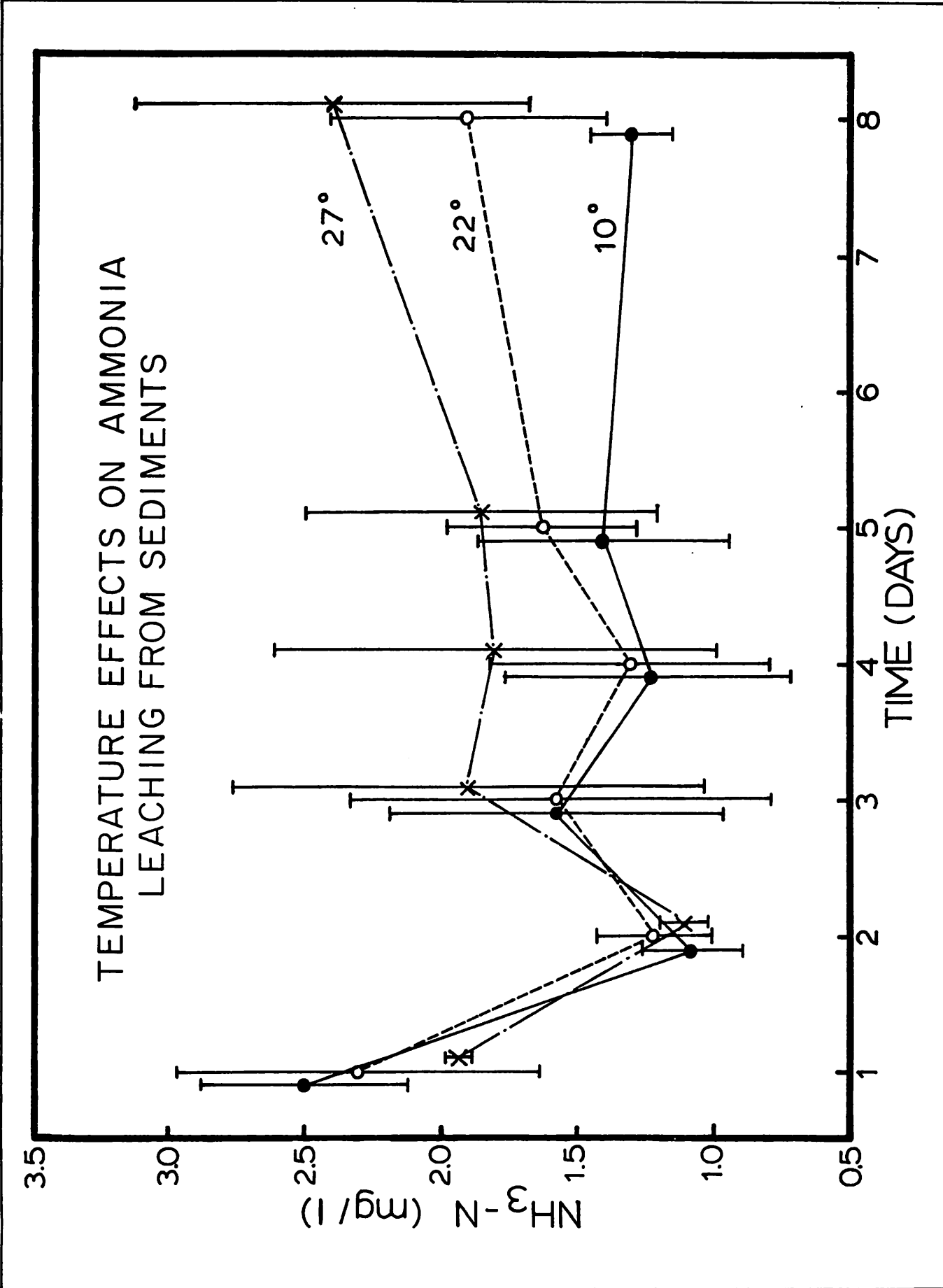
EFFECTS OF SALINITY ON AMMONIA UPTAKE BY SEDIMENTS

Figure IV-19
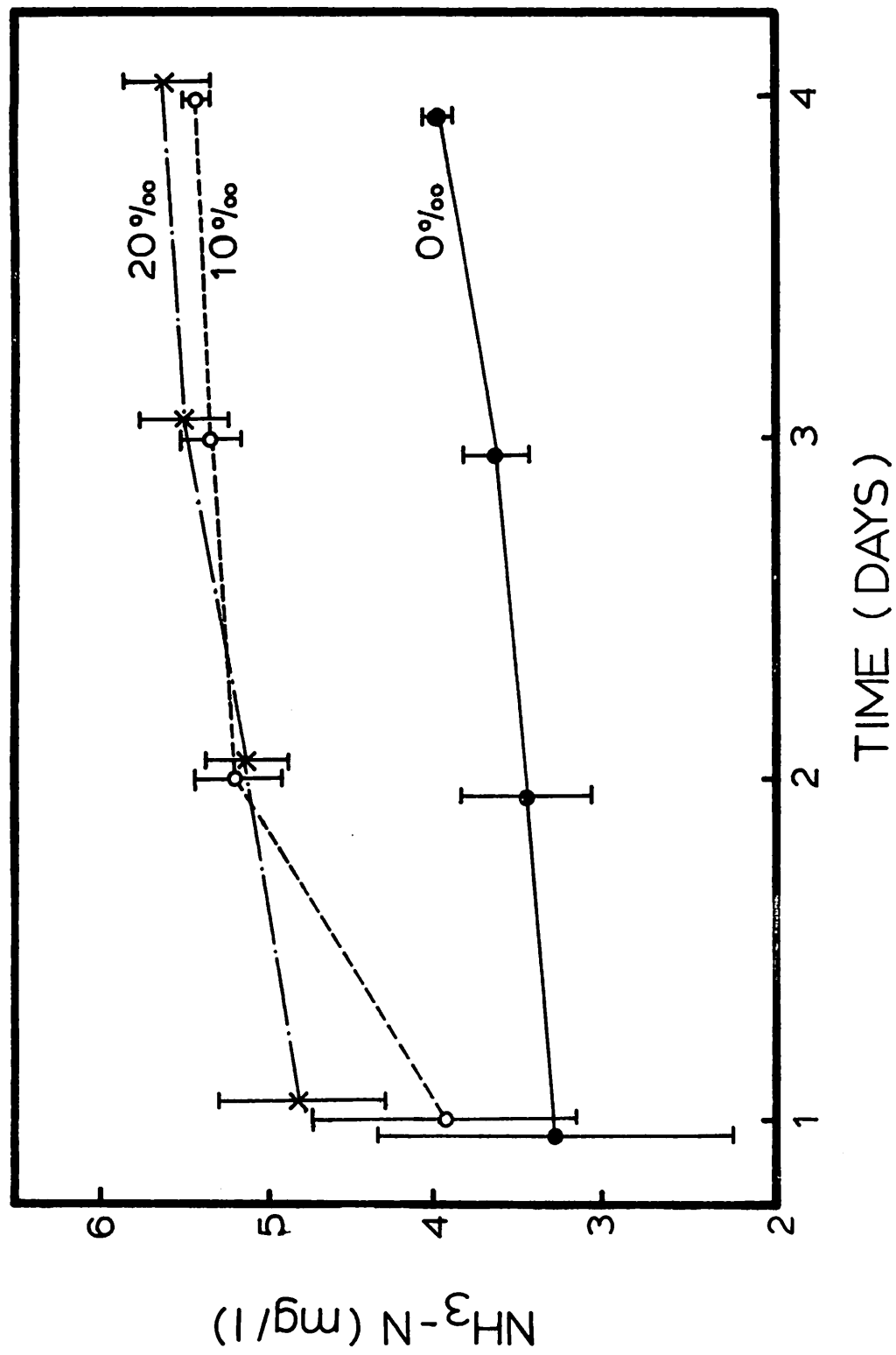
EFFECTS OF TEMPERATURE ON AMMONIA UPTAKE BY SEDIMENTS
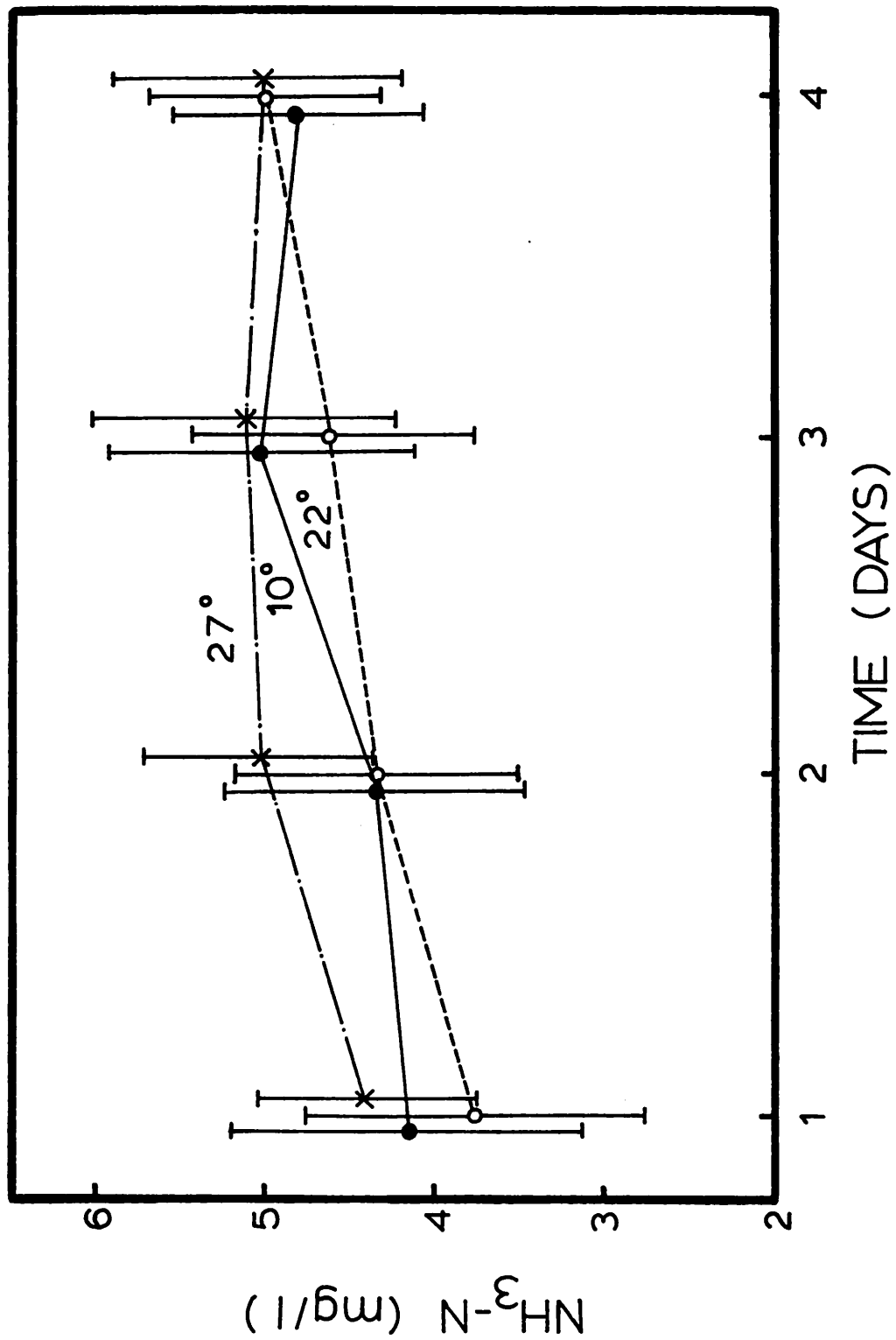
Amounts (mass) of ammonia removed from the system during the leaching experiments and taken up during the uptake tests may then be expressed on a cumulative basis through time (Figures IV-20 and IV-21 respectively). These data are expressed as mg NH_3-N leached or taken up per m^2 using the core sediment surface area as the appropriate divisor.

Exchange Rates

In order to investigate more thoroughly interactions of parameters measured and their respective effects on leaching and uptake processes, data collected were entered into a stepwise multiple regression computer program of the following general form:

$$\ln y = a + b_T x_T + b_t x_t + b_s x_s + b_{c_o} + x_{c_o} + \ldots + b_n x_n$$

where

$\ln y$	= the natural logarithm of any nutrient ("y") either sorbed or leached expressed as mg Y/m^2
a	= a constant
$x_T, x_t, x_s, x_{c_o}, \ldots, x_n$	= the independent variables temperature, T (^oC); time, t (days; salinity, s (%o); initial concentration of the nutrient in the water column, c_o; and an nth variable respectively, and
$b_T, b_t, b_s, b_{c_o}, \ldots, b_n$	= the respective coefficients for the corresponding independent variables.

In addition, any interactions between variables could be delineated using an analysis of variance and a correlation matrix.

Leaching data (as cumulative mg/m^2 leached, the data shown in Figures IV-20 and IV-21) was entered into the regression model with the independent variables of time, temperature, and salinity. Both time and salinity were significant ($p < 0.005$ and $p < 0.01$ respectively) with positive coefficients. Temperature, however, was not significant ($p > 0.10$). The following model resulted:

$$\ln y = 4.406 + 0.408 \, x_t + 0.028 \, x_s. \qquad \text{(IV-2)}$$

Similar results were found with uptake data for ammonia:

$$\ln y = 6.435 + 0.200 \, x_t - 0.029 \, x_s. \qquad \text{(IV-3)}$$

Here salinity is inversely related to uptake and the same order of magnitude. Table IV-5 summarizes pertinent multiple regression statistics.

Figure IV-20

SALINITY EFFECTS ON AMMONIA
LEACHING FROM SEDIMENTS

Figure IV-21
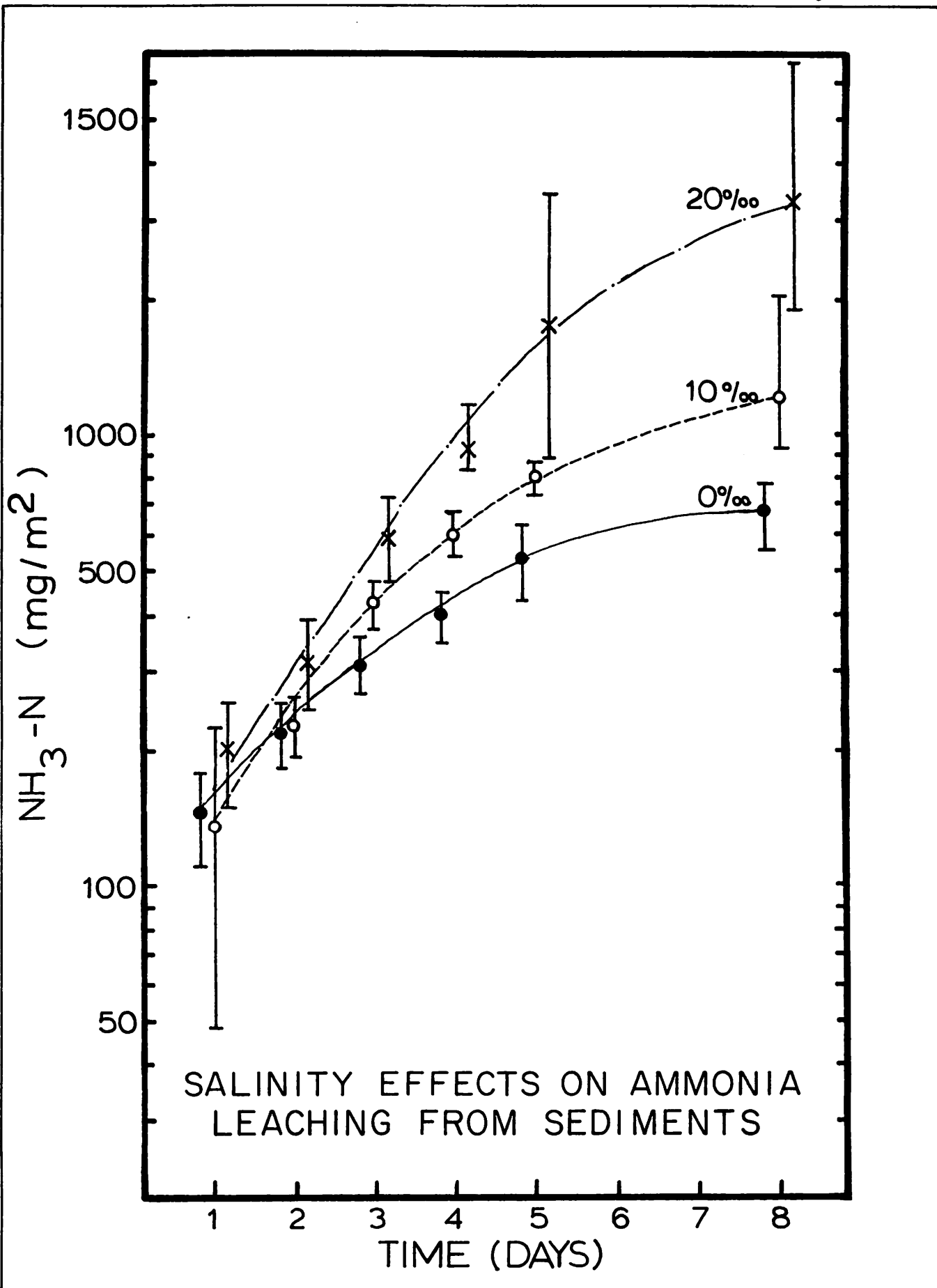
SALINITY EFFECTS ON AMMONIA
UPTAKE BY SEDIMENTS
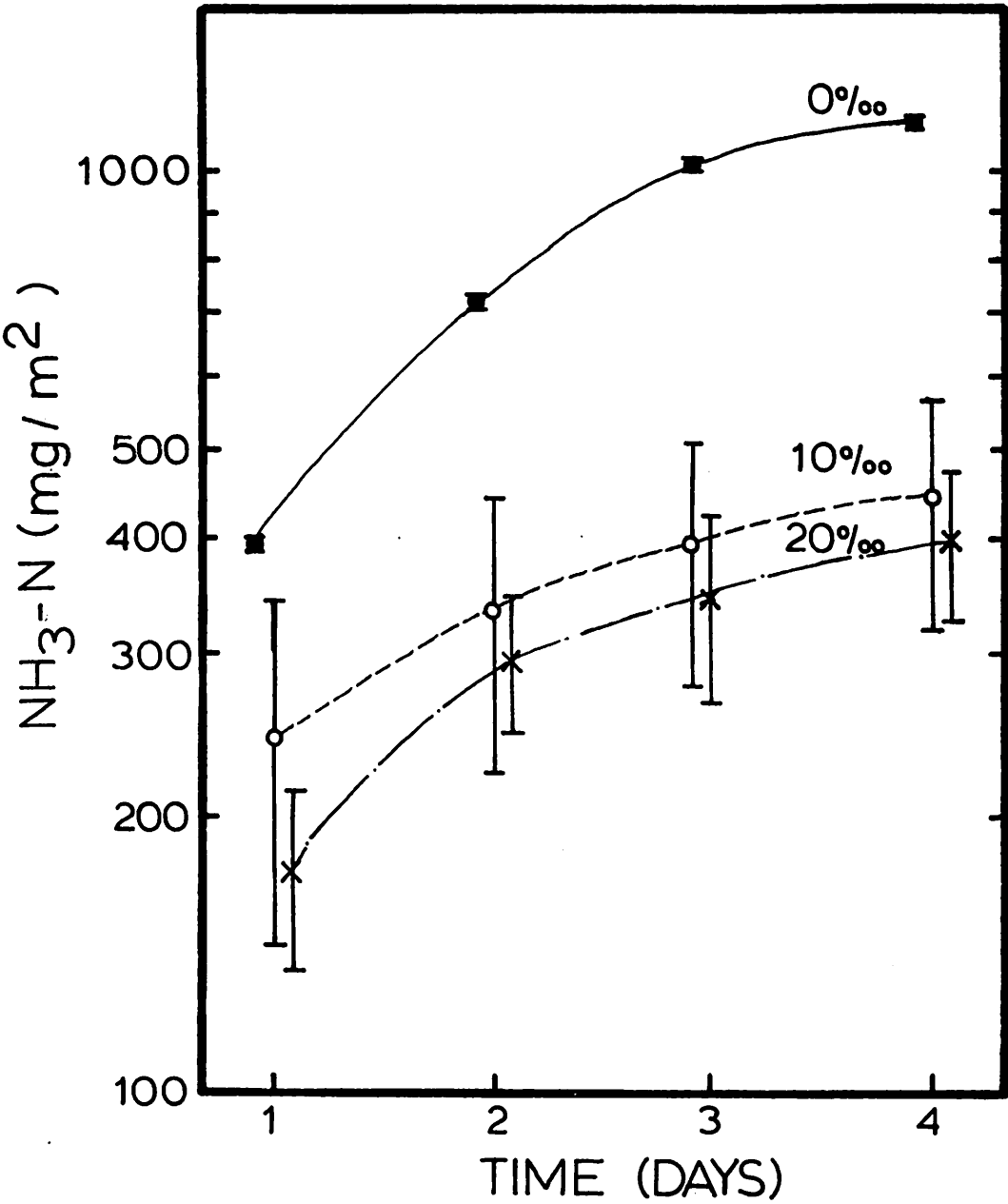
TABLE IV-5

MULTIPLE REGRESSION STATISTICS

Equation #	N	Mult. Reg. Coefficient	Std. Error of Estimate	Std. Error of Regression Coefficients (Sb_n)							
				S_{b_t}	P	S_{b_T}	P	S_{b_s}	P	$S_{b_{c_o}}$	P
IV-2	60	0.933	0.244	0.022	< .001	NS*		0.004	< .01	NA**	
IV-3	40	0.898	0.185	0.021	< .001	NS		0.004	< .01	NA	
IV-4	12	0.673	0.065	NA		NS		0.002	< .10	NS	
IV-5	12	0.748	0.051	NA		.003	<.10	NS		NS	

*NA meaning not available or not entered
**NS meaning not significant (P > .05)

In order to examine effects of various parameters on the rates of cumulative leaching and uptake, a "best" line (sum of squares method) fit was determined for each core individually for each experiment. Only the first five days of data were included for leaching as it appeared that the slopes between the fifth and eighth days were generally significantly lower (see Figures IV-16 and IV-17). This may have been due to an approach to equilibrium conditions or this may in part have been an artifact of the experimental procedure. By calculating the slope of the line a rate of leaching (in mg nutrient/m^2/day) for each core was established. As it was suspected that rates of leaching could be effected by the initial concentration of the nutrient in the water, the twelve cores involved in the first leaching experiment were analyzed as a group.

Rates of leaching and uptake calculated as described above were regressed against the independent variables of temperature, salinity, and the initial concentration of the overlying water. For leaching experiments, the following regression equation resulted:

$$y = 0.3085 + 0.0066 \, x_s. \qquad \text{(IV-4)}$$

where:

y = rate of cumulative leaching (mg NH_3/m^2/day), and

x_s = independent variable of salinity (ppt).

Salinity was found to be significant at the 10 percent level of probability. Other independent variables were not significant ($p > 0.10$). Likewise rates of cumulative uptake were regressed against the same independent variables as above yielding the following equation:

$$y = 0.1491 + 0.0084 \, x_T - 0.07846 \, x_{c_o}. \qquad \text{(IV-5)}$$

where:

y = rate of cumulative uptake (mg NH_3/m^2/day),

x_T = mean temperature value over the five day period, and

x_{c_o} = initial concentration of the water column.

Temperature and the initial concentration are barely significant at $p < 0.10$. Salinity was not significant although it was found to be correlated with the initial concentration of ammonia in the overlying water.

As can be seen from Table IV-5 neither of these equations show very significant correlations. Trends are indicated, however, which need to be verified by increasing the sample size.

Data analysis on nitrate and phosphate was not completed due to delays in receiving results from the State Health Department Laboratory. Nitrate levels during the first set of leaching and uptake experiments were quite low, generally less than 0.03 mg NO_3-N/l. Any increases in these levels were short-lived dropping to their former levels within twenty-four hours. This was not true, however, of a few cores during the second phase of leaching. These cores show initially a very high concentration of NO_3 in overlying water with accompanying low concentrations of ammonia, indicating possible biological denitrification. Phosphate exchange patterns were obscured by erratic behavior, a situation found by other investigators (Pomeroy, et al., 1965).

Marsh Reactor Studies

Flow Conditions

Flow into the reactors was measured at 0830 and 1630 each day and read-justed, if necessary, to approximately 14 ml/min. However, the gravity-feed siphon system for inflow water did not maintain uniform flow, since particulate matter often clogged hose constrictions where clamps were placed. Water levels were not always constant within the reactors because floating algae mats would block the overflow tube and the water level would rise. Actual water input rates ranged from 0-60 ml/min, although mean flows generally occurred within ± 10 ml of the standard flow. These variations upset the daily exchange rate which should have provided 10 complete water exchanges through each system, or a detention time of 0.1 days.

Water Quality Conditions

Since the reactors were installed outside to take advantage of the intense summer sunlight, the model systems were exposed to take advantage of the intense summer sunlight, the model systems were exposed to optimum photosynthetic conditions as indicated by large dial fluctuations in dissolved oxygen and pH. Daytime pH conditions fluctuated from less than 8.0 to more than 10.0 within the reactors as CO_2 was assimilated rapidly by the system autotrophs. Dissolved oxygen concentrations varied most spectacularly for Reactors 1, 2, and 3 which contained dense algal mats. Reactors 4, 5,

and 6 had emergent vegetation along with epiphytic and benthic algae growth and did not exhibit such radical daily changes. In the morning, algal mat reactors had ambient concentrations of dissolved oxygen as low as 2-3 mg/l, but often exceeded 15 mg/l (the maximum measurable level on the YSI probes used) after 8 hours of sunlight. Since their morning oxygen values were generally higher (4-6 mg/l dissolved oxygen), the reactors with marsh plants only showed daily increases of 6.6 to 10 mg/l. Significant loss of oxygen could be expected from these super-saturated systems due to diffusion. This problem, in association with oxygen probe limitations at high dissolved oxygen levels, prohibits reasonable productivity estimates.

Diurnal temperature patterns reflected significant daytime heating, even though this problem was minimized by placing the reactors in a water-filled pool that served as a constant-temperature water bath. Influent marsh water from the partially-covered wooden boxes was consistently cooler than the reactor effluent. Morning temperatures (0830 hrs) of the reactor water ranged from $25-28^{\circ}C$; however, afternoon temperature readings generally exceeded $35^{\circ}C$ ($33.7-41.5^{\circ}C$).

Data on carbon nutrient exchange (TOC and VSS) for the marsh reactors was limited to two consecutive days. Standing water in the reactors consistently exhibited higher carbon concentrations than were introduced in the influent water. Some changes in ambient carbon concentrations occurred during the day, but the data record was not sufficiently long to predict a diurnal periodicity of organic carbon production, consumption, and export.

The production and net export of organic nitrogen was apparent for all reactors, regardless of the dominant system producer (algae or emergent plant). In addition, no differences in organic nitrogen concentrations were evident for model systems receiving either nutrient-enriched or untreated water. No obvious pattern of diurnal fluctuation emerged for this nutrient species.

Other nitrogen nutrient species (ammonia, nitrite, nitrate) demonstrated a net loss to the rapidly-growing microcosm communities. Untreated influent marsh water maintained favorable but low ambient concentrations, and and the reactor water had minimum detectable levels throughout the entire experimental period. Enriched water flowing into some systems had been spiked initially to provide 5 mg NH_3-N/l; however, this ammonia concentration was nitrified continuously in the reservoir supply box, so that

considerably less was actually available in the influent. At the same time, nitrate concentrations in the enriched influent rose during the test period.

Concentrations of total phosphorus and orthophosphorus remained stable in the supply reservoir, regardless of the prevailing water condition (enriched or natural). Total and orthophosphorus levels in the spiked reservoir ranged ranged from 2.9-3.7 mg/1, even though only 2 mg PO_4-P/1 was the target concentration. Natural marsh water had nutrient levels approximately 30 times less than the enriched water. Due to uptake by the microcosm communities, phosphorus levels (both forms) in the reactor standing water were lower than the influent concentrations.

CHAPTER V

DISCUSSION

FIELD INVESTIGATIONS

The water exchange between the marsh and Swan Lake occurs in response to tidal influences. Flooding tides carry Swan Lake waters into the marsh, while an ebb flow partially drains the marsh. Stage of the water depth in bayou channels varies in response to daily tidal fluctuations, as well as hydrologic conditions in the adjacent estuarine areas (i.e. decreased river flow, strong changes in wind direction, and velocity). No direct inputs of Lavaca River water into the marsh were noted during the field sampling, although increased river inflow would probably breech the low natural levees along the river and flood the back of the marsh.

Prevailing hydrologic conditions in the marsh differed during each visit to the Swan Lake system. Three initial reconnaissance trips to the experimental area (one by helicopter) were made in early June when abnormally high tides had completely flooded the marsh. Continually receding water levels were encountered on subsequent sampling trips. For instance, the first field trip (June 28-29) occurred under flooded conditions (marsh vegetation inundated during both flood and ebb periods), whereas during the third sampling session (July 30-Aug. 1) water in the marsh was restricted to the bayou channel and major tributaries (vegetation was entirely emergent). The second experimental period (July 11-12) represented an intermediate hydrologic condition where a flooding tide left vegetation partially submerged and ebb generally resulted in exposed sediment.

Weather conditions in the Lavaca Bay area remained relatively constant throughout the summer. Although light local showers were noted on occasion, a chronic drought persisted over this portion of Texas, and it was not broken until after the termination of field sampling. The wind appeared to have some effect on the magnitude of tidal inundation as strong southeastern breezes pushed additional water into Swan Lake and winds from the north produced the opposite effect (decreased marsh water exchange). Decreasing river inflow due to the lack of precipitation in the Lavaca-Navidad basins may have been primarily responsible for the overall water level changes observed.

Changes in water quality parameters, such as dissolved oxygen and temperature, follow a normal diurnal pattern, but it may be disrupted depending

upon the source of the water. Diurnal curves tended to become steeper as the water level dropped and biological activity became more concentrated. Strong oxygen demands from the sediments (both algal and bacterial respiration)rapidly removed oxygen from the marsh water during the nighttime, although flood tides sometimes renewed the supply with oxygenated Swan Lake water. Extensive algal production during the day was capable of raising the in situ oxygen level far above saturation.

The dense growths of algae and rooted vegetation in the marsh provide a rich source of organic-based nutrients. Decomposition of dead plant material provides various grades of particulate and dissolved organic matter and nutrients for support of intra-marsh consumers and transport to adjoining estuarine systems. The rapid decomposition implied by the observed oxygen demand and supplied the organic carbon, organic nitrogen, and ammonia that were generally transported out of the marsh. Ambient concentrations of these degradation products fluctuated with the direction of flow, especially with low water levels in the marsh, decreasing when Swan Lake waters entered the marsh and increasing as ebb flows drained the area. Inorganic nitrogen forms (NO_2, NO_3) remained at low levels during all field trips regardless of the origin of water being sampled. The reduced state of marsh sediments may have inhibited production of these oxidized nutrients, but more likely the algal mats and attached algae removed these forms as they became available in the marsh.

For the first two field trips when water level was moderately high, orthophosphorus levels exhibited only slight variation in response to flow direction changes. Total phosphorus measurements, which include a sizeable organic-related component, responded more like other degradation products, increasing in concentration with the exodus of marsh water. When the plants were totally emergent during the July 30-August 1 sampling trip and completely relied on soil-associated phosphorus, levels of both forms tested showed distinct pulses related to the stage of the tidal cycle. Thus, leaching of phosphorus from the sediments may be an important and major source of phosphorus for attached and benthic algae in the marsh.

Mass balances for the various nutrient species show that the marsh under study acts as a source of nutrients for the Swan Lake and upper Lavaca Bay systems. Although the quantity of outward material flow differs with marsh hydrologic conditions, water moving through Station 1 on the main

bayou always carried more nutrients out during ebb flow than were brought in during the preceding flood period. This evidence appears to justify the role of this marsh as a net exporter of nutrients.

The outward movement of organic-based substances is greatest, particularly carbon (measured as TOC or VSS) and organic nitrogen; total phosphorus is exported to a lesser extent. Observed difference in mass transport between ebb and flood portions of the tidal cycle have amounted to as much as 112 kg of total organic carbon or 214 kg of volatile suspended solids (see Tables IV-2, 3, and 4). The mass flow of organic nitrogen compounds out of Swan Lake marsh ranged from 1.6 to 10.9 kilograms per tidal cycle. Inorganic nutrients (NH_3, NO_2, NO_3, and orthophosphorus) rarely exceeded a 0.5 kg mass transfer difference, and the difference often amounted to only a few grams. Further, the nitrite and nitrate were always at minimum detectable concentrations. This would imply that the marsh does not actively take up inorganic nutrient species from incoming estuarine water, or these nutrients are removed rapidly in the marsh and in Swan Lake causing their concentrations to be low continually. The latter situation is the most likely.

It is interesting to note that the highest export of TOC and organic nitrogen occured when the water levels were highest and lowest, and the lowest export occured with water levels under more or less normal water levels. The attached algae and algal mats slough after drying and are transported easily even under low water conditions with minimum inundation. Flood conditions following a dry period would also dislodge and transport this material in large quantities out of the marsh. For the first two sampling periods conducted in this study, a reduction in exported material with the decrease in water level would be expected; the large export during the dry period would also be expected. Marsh areas experiencing periodic drying and flooding may be adapted to export material in this manner.

LABORATORY INVESTIGATIONS

Fixed-Bed Investigations

Data from the core experiments indicate the complexities involved in leaching and uptake exchange processes. The good correlations between ammonia mass leached and sorbed versus time indicate fairly steady rates over a four to five day period, but leaching of ammonia from marsh sediments

is shown to proceed at a much faster rate than uptake. However, this pattern is to a large degree influenced by salinity. Increasing salinity enhances cumulative leaching and likewise depresses cumulative uptake. Although no significant effect of salinity on rates of leaching or uptake was shown, this may be due to the small sample size at each salinity and temperature.

If salinity does have a significant effect on nutrient exchange, anthropogenic or natural alterations of salinity regimes affecting the river-marsh-estuary complex should be thoroughly reviewed. Comparative studies involving different systems and concerning mass and energy flows through these systems would be highly desirable.

Marsh Reactor Studies

The marsh reactors served as adequate physical models of the Swan Lake marsh community. Emergent plants (Scirpus maritima macrostachyus) collected with the original cores continued to thrive and some plants even bloomed during the late summer experimentation. Dense benthic algae mats grew in all marsh reactors during the developmental phase when nutrient-rich marsh water was continuously added. During the experimental phase, the reaction of algae to nutrient inputs could be ascertained visually. Algae mats turned bright green in color when enriched water was fed into the reactors, while "natural" marsh water produced olive-colored algae.

Clogging problems within the water supply system resulted in extremely variable daily flow rates into the reactors. Even though mean flows between readjustments were fairly similar, the lack of consistent flow measurements makes the construction of a nutrient mass balance difficult. In addition, volume changes due to clogged reactor ports permitted excess nutrient availability to community autotrophs.

Abundant summer sunlight provided excellent conditions for photosynthesis within the reactors. Large diurnal fluctuations in dissolved oxygen and pH demonstrated the rapid rates of production and assimilation for the essential photosynthetic gases. In fact, primary production by the benthic algae mats introduced too much oxygen to be accurately measured by the YSI oxygen probes employed for such analysis. Due to the nature of the sampling program (only two samples per day), this problem precluded reasonable estimates of community metabolism via the diurnal curve method.

Although water quality measurements were collected over a 10-day period, the continuous data record was limited to 2-3 days. Still, some trends were evident for the various nutrient parameters. Net export of organic nitrogen was obvious throughout the study period. All other nitrogen forms (NH_3, NO_2, NO_3) appeared to be taken up by the reactor autotrophic communities, as did both forms of phosphorus. The data on carbon inputs and outflows was not sufficient to demonstrate the direction of exchange, although one would expect the rapidly-growing autotrophs to release excess dissolved organics which could be transported out of the microcosms.

Maintenance of a particular enriched nutrient level in the reactor water supply was not as straightforward as originally thought. Some biological activity in the supply reservoirs, as indicated by diurnal dissolved oxygen changes, could utilize some inorganic nutrients for photosynthesis, as well as release others through decomposition. Phosphorus concentrations were relatively stable in the reactor influent throughout the study period, although this level was higher than the proposed concentration. The water supply enriched with ammonia exhibited a different pattern. Ammonia levels dropped continuously, while the nitrate concentration increased simultaneously. Apparently, ammonia was being oxidized, so that uptake by reactors must be considered in terms of both nutrient types.
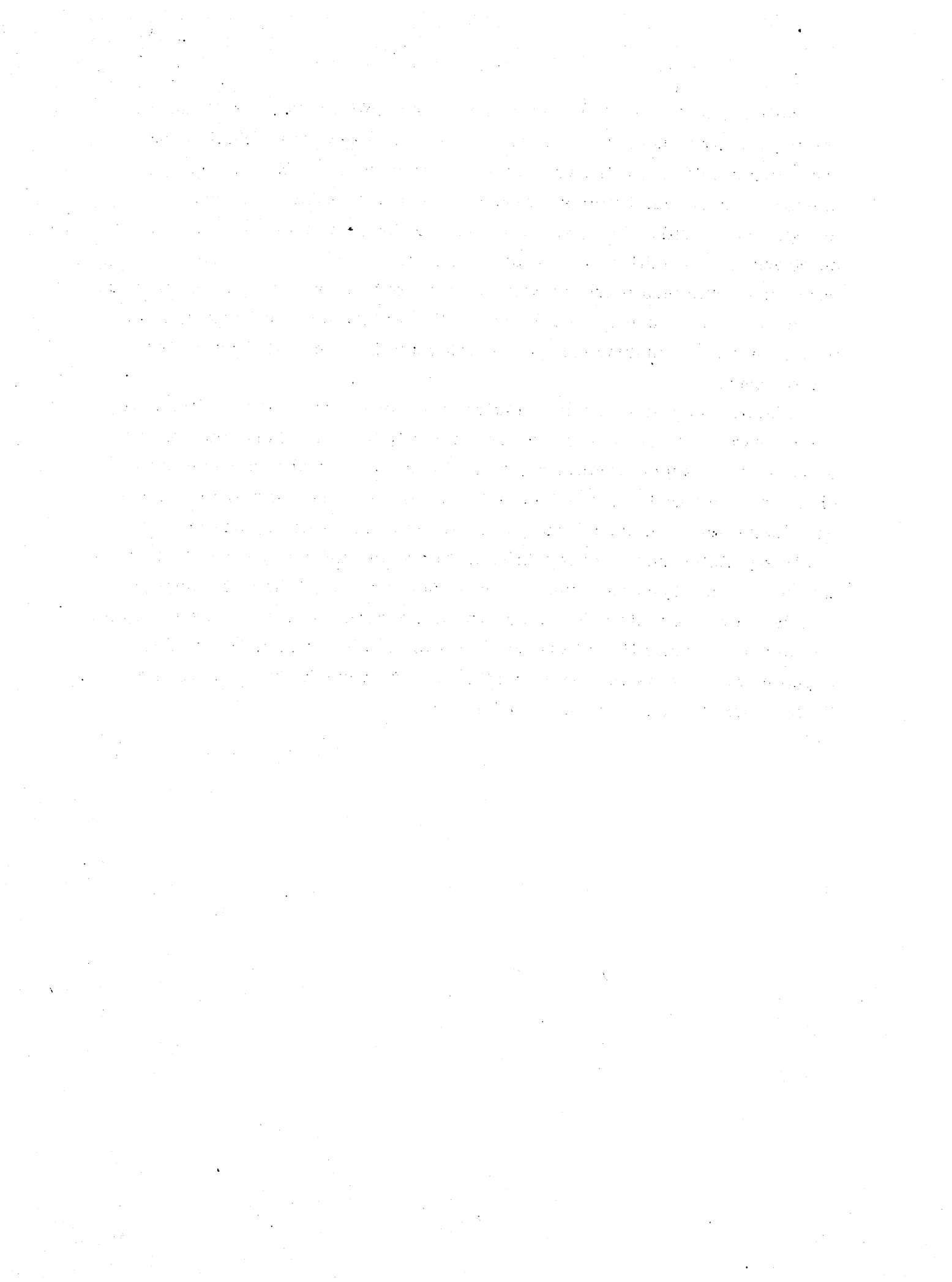
CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Despite the brevity of this study and the difficulties encountered in the laboratory work and nutrient analysis time schedule, several important conclusions may be drawn from the results as follows.

Field Studies

1. The study area in Swan Lake marsh acts as an oscillating-flow system; Swan Lake serves as one water source, while the large bi-lobed ponds and numerous pot-holes in the interior marsh area contain a large portion of the marsh water supply. Since one major bayou drains this entire region, Station 1 effectively monitors the total water and nutrient exchange.

2. The hydrologic regime is essential to the mass transport of nutrient material from the marsh to adjoining estuarine areas. Local tides provided the prime mechanism for water movement through the marsh system during the period of study (June 28–August 1, 1974). However, overall water stage will also vary with changes in river flow and the wind-generated seiches in the upper Lavaca Bay system.

3. Nutrients derived from the degradation of organic matter show the greatest exodus from the marsh. Various carbon forms (both measured as TOC and VSS), nitrogen as organic nitrogen and ammonia, and total phosphorus (organic component) are produced rapidly following the death of emergent vegetation or algal mats. Ambient concentrations of these nutrients generally rise during the later stages of ebb flow as they are flushed out of detritus on the sediment surface.

4. The low concentrations of nitrite, nitrate, and orthophosphorus in both flood and ebb tide waters indicates that marsh vegetation, mainly attached and benthic algae, is removing these nutrients as soon as they become available from whatever source. Indeed, those nutrient forms may be limiting in the marsh. Emergent plants, which must face alternating periods of partial submersion and air exposure, appear to obtain their nutrient requirements from sediments.

5. Computation of aquatic primary production by the diurnal curve method is drastically limited by the presence of additional sources and sinks for dissolved oxygen in the marsh. High sediment oxygen demand, changes in water mass oxygenation (due to origin of water mass), and oxygen supersaturation generated by rapid phytosynthetic activity all inhibit the application of this method. Even under optimum conditions, the diurnal method would only account for production due to submerged benthic, mat, and epiphytic algae. Measurement of the growth and production rates for the emergent saltmarsh bullrush was not attempted within this phase of the project.

6. Periodic drying of the marsh area studied may be an important mechanism for enhancing organic nutrient release. Plants in this marsh, especially the algal mat, are adapted for periodic drying, high temperatures, and a widely varying salinity regime; high waters (flood conditions) tend to flush sloughed mat materials from the marsh as well as to revive the mat, low waters permit drying and sloughing, and normal water levels permit a steady but reduced exchange of nutrients from the marsh.

Laboratory Studies

Fixed-Bed Sediments

1. Ammonia was released from the sediment surface in the core reactors at a high rate. The rate of release increased with salinity ranging from 90 mg NH_3-N/m^2/day at O ppt to 500 mg NH_3-N/m^2/day at 20 ppt.

2. Ammonia was taken up by the sediments at a slightly lower rate than released; the uptake rate was inversely dependent on the salinity of the overlying water ranging from 45 mg NH_3-N/m^2/day at 20 ppt to 325 mg NH_3-N/m^2/day at 0 ppt.

Marsh Reactor Studies

1. The marsh reactors served as adequate physical and biological models of the Swan Lake marsh community. The algal mat and emergent vegetation in the reactors survived and grew well.

2. In the uptake studies organic nitrogen was exported from the reactors as it is in the field while ammonia, nitrite, nitrate, and phosphorus were removed by the vegetation in the reactors, again as is the case for the field.

RECOMMENDATIONS

Field Investigations

1. The investigation of nutrient exchange in the Swan Lake marsh should continue to better define the rates of net nutrient export and the influence of water level and dry periods on these rates. Similar studies should be done elsewhere on the Texas coast to delineate the differences between marsh structure and function in "water rich" areas and "water poor" areas. Different techniques may well be needed to manage marshes in these different areas.

2. Future nutrient export studies should be coupled with marsh productivity studies to better define the sources and sinks of organic and inorganic nutrients. Such studies should be conducted for a variety of water level conditions and over several tidal cycles to dampen erratic water level fluctuations.

Laboratory Investigations

Slurry Tests

1. The nutrient uptake and release tests data should be analyzed and presented in the final report for the continuing study on nutrient exchange in the marsh reactors. They should also be used to direct further investigations.

2. The effects of pH and a wider range of salinity than used in these tests should be investigated as well as the effects of drying.

Fixed-Bed Tests

1. A portion of the results for these tests are yet to be analyzed and should be presented in the final report for the continuing studies.

2. Continuing studies should emphasize development of terms for the nutrient exchange model, namely:

a. Isotherms should be developed to relate sediment nutrient concentrations to those in overlying water at equilibrium under varying temperature and salinity conditions;

b. Uptake and release of nutrients from the sediments in the cores should be carried out in a stirred, flow-through reactor to obtain rate data;

c. The mass transfer coefficient for each nutrient should be calculated using the above information.

3. The influence of drying on the mass transfer coefficient should also be investigated.

Marsh Reactor Tests

1. The marsh reactors should be moved to an indoor location so that light and especially temperature can be controlled. Also, water flows should be metered in by a pump rather than by gravity flow to obtain more consistent flow rates.

2. Nutrient exchange studies should continue with the following objectives:

a. To determine nutrient exchange rates for systems with emergent vegetation and attached algae and those with algal mats;

b. To determine nutrient exchange rates with continuous (flood), intermittant (tidal), and low (drought) flows under different temperature and salinity conditions;

c. To determine the comparative magnitude of the various nutrient sources and sinks in the marsh system, namely emergent vegetation, attached algae, algal mat, and sediment.

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PART II:

THE ROLE OF PLANTS IN NUTRIENT EXCHANGE
IN THE LAVACA BAY BRACKISH MARSH SYSTEM

by

Anita J. Dawson and Neal E. Armstrong

August 31, 1975

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CHAPTER 1

INTRODUCTION

NEED FOR STUDY

Estuaries are known to be highly productive areas. They are often more productive than adjacent saltwater or freshwater areas and serve as nursery grounds for neritic species. The saltwater marsh is an important component of the estuary, contributing organic and inorganic nutrients to the waters which enables them to support such an abundance of life.

Several studies of saltmarshes on the eastern coast have been done but little work has been done to date on the Texas saltmarsh system in regard to productivity, the effects of freshwater and tidal flows, or nutrient cycling. A mathematical model of the Lavaca River – Lavaca Bay – Matagorda Bay ecosystem is being developed by the Texas Water Development Board to enable the assessment of the possible impacts of water resources development in the Lavaca River and Garcitas Creek basins. A preliminary study of the cycling of nutrients in the Lavaca Bay saltmarsh has been done to provide information on the exchange rates (of nutrients) which occur in the marsh (Armstrong et al., 1975). This work included field and laboratory studies of the nutrient exchanges occurring, but additional work was shown to be needed to further define the role of the plants of the saltmarsh in this important cycling process.

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OBJECTIVES

This study was undertaken to determine the role of plants in
nutrient exchange in the Lavaca Bay saltmarsh. The exchange was
studied at two water levels and at two concentrations of nutrients
(low and spiked) in the influent water to determine the rate of
nutrient exchange and to determine the magnitude of nutrients con-
tributed by the various components of the marsh system. Since
periods of drying occur in the Lavaca Bay saltmarsh during the summer,
the effects of drying on the exchange of nutrients also was determined.

SCOPE

Laboratory tests were conducted on two algal mat community and
four marsh grass community microcosms. (In two of the marsh grass
systems the sediments were covered by a layer of paraffin essen-
tially sealing them from the overlying water. By so doing the con-
tributions of the emergent vegetation to the exchange were determined.)
Constant flow was maintained through each microcosm at a rate simu-
lating the diurnal effects of the tides and all microcosms were stirred.

Nutrients were added to half of the microcosms in low concentra-
tions and to the remaining half in higher concentrations. Samples
of the water in each of the microcosms were taken periodically and
analyzed for various forms of carbon, nitrogen, and phosphorus.
Mass balances were computed to determine the exchange of each of
the nutrients by the various communities. In order to determine the
effect of dessication on the exchange rate the microcosms were dried

for a period of time, then reinundated with water and samples were
again taken periodically.

CHAPTER 2
LITERATURE REVIEW

INTRODUCTION

Nutrient cycling in saltwater marshes has been found to be very complex due to the interactions of the many marsh components as well as the influences exerted by freshwater and tidal flow. The components of the area include: plants (marsh grasses, algal mats, phytoplankton, and diatoms); bacteria; animals (zooplankton, crustaceans, molluscs, and insects); the overlying water column; and the sediments. The species of plants and animals present in a marsh are strongly influenced by several variable factors such as pH, salinity, meteorological conditions, succession, and nutrient availability. Biological, physical, and chemical interactions among the plants, animals, sediments, and the overlying water column are the primary components contributing to the constant cycling of nutrients in the saltwater marsh (Keeney, 1973; Zobell, 1946; Pomeroy et al., 1972; Armstrong et al., 1975).

Little work has been done to date on nutrient cycling in the saltwater marsh ecosystem as a whole. However, many studies have been done concerning nutrient cycling within various components of the system.

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The first section of this chapter will consider studies concerning marsh grasses; the second, studies of algae and algal mats; the third, suspended organisms; the fourth, the sediments; and the fifth, the saltmarsh ecosystem.

MARSH GRASSES

The grasses (emergent vegetation) in the Lavaca Bay saltmarsh are normally partially submerged. The amount of direct contact that they have with the water varies with the tidal fluctuations of the area. During the summer months there are periods during which the water level recedes considerably leaving the vegetation completely emergent (dry).

Productivity

Several factors have been found to influence the productivity of the macrophytes of the saltmarsh. Light intensity, temperature, and nutrient availability are known to be important factors in plant productivity. Plants of the saltmarsh are also influenced by salinity and variations in both tidal and freshwater flow. These plants can normally tolerate fluctuations in both salinity and temperature. Zostera marina, a completely submerged seagrass, can exist in waters with salinities from 0 ppt to 56 ppt (maximum productivity occurs at 36 ppt) and temperature ranges of -6°C to 40°C (Biebl and McRoy, 1971). Spartina alterniflora can withstand salinities of 40 ppt - 50 ppt (Hoese, 1967). Gross photosynthesis increases with temperature to 35°C and then decreases sharply.

In marshes, the growing season of the plants is longer than it is for cultivated crops. This contributes to the higher production of marsh areas when compared to terrestrial communities. In addition, plants in the marsh have become well adapted to the extreme conditions of anaerobic soil (Laing, 1940). Another reason for high productivity is the vertical orientation of the leaves of most marsh plants. This reduces intense heating, exposes the maximum leaf surface to sunlight and minimizes neutral shading (Jervis, 1964). The plants in marsh areas have an abundant supply of water in the soil as well as the water flowing past (under inundated conditions) which supplies more nutrients than standing water (Schelske and Odum, 1961) and supports greater productivity. The marsh plants, as obstructions of water flow, trap and retain nutrient-rich particles in the marsh area (Blum, 1969; Ranwell, 1964). Enough phosphorus was present in the sediment of one _Spartina alterniflora_ marsh to support growth for five hundred years (Pomeroy et al., 1969). In the salt marshes of Georgia and Delaware, the water flooding the marsh is the ultimate source of nutrients (Odum and de la Cruz, 1967; Reimold and Daiber, 1970). Net production of a _Spartina alterniflora_ marsh in Georgia was measured by Odum (1959,1961) and found to range from 2000 - 3300 g (dry)/m^2/yr. The biomass of a Texas _Typha latifolia_ and _Typha domingensis_ community was measured and determined to be 3982 g (dry)/m^2 (McNaughton, 1966).

Spartina alterniflora marshes have been found to be highly productive and have a photosynthesis to respiration rate greater than one (Teal, 1962). This excess production is an important nutrient source for surrounding areas (Odum and de la Cruz, 1967). This is supported by Teal's (1962) work in which he found that approximately

45% of the production of a Georgia Spartina marsh was exported to surrounding waters.

The salt marsh plants are the primary producers supporting two food chains. In the first, the primary consumers feed directly on growing plants and in the second, detritus of marsh plants supports the primary consumers (Keefe, 1972).

Boyd and Hess (1970) studied correlations between nutrient level and shoot production in Typha latifolia (bulrush). A positive correlation exists between standing crop and the concentrations of dilute acid-soluble phosphorus in hydrosoils and dissolved phosphorus in waters. The concentrations of most nutrients in plant tissues are positively correlated with nitrogen content. Standing crop is the decisive factor in determining the quantities of nutrients in a given area.

Grasses are important as primary producers of the estuarine marsh. In the Gulf, productivity of the attached algae has been found to be only a small fraction of that of the grasses (Humm, 1956). In considering marine plants for aquaculture, Stengel (1974) also found macrophytes to be considerably more productive than algae.

Nutrient Absorption

McRoy and Barsdate (1970) in working with the completely submerged marine grass, Zostera, found that it is capable of absorbing ^{32}P through both its leaves and its roots. Absorption of ^{32}P by the

roots led subsequently to its release to the surrounding waters by the leaves. Once in the surrounding waters this phosphorus is available to epiphytic and benthic algae, which are primarily responsible for the removal of phosphorus from marsh waters (Pomeroy, et al., 1972). The reverse of this process was also found to occur but was of less intensity. The relative concentrations of phosphate in the water and in the sediment were found to be the factors determining the direction of translocation of ^{32}P by the plants. In further work, the cycling of phosphorus was studied in the eelgrass ecosystem of Alaska (McRoy, Barsdate, and Nebert, 1972). Translocation of phosphorus from sediments to water by the eelgrass was determined to occur at a rate of 62.4 mg P/m^2-day. In addition to the phosphorus released through the leaves, export of floating eelgrass was estimated to contribute 25.86 mg P/m^2-day to the nearby sea. In later studies, Reimold (1970) found the salt marsh cordgrass, Spartina alterniflora, to act in the same way. The nutrient flux from sediment to water was determined to be at a maximum during the summer months and at a minimum during winter indicating an association with productivity of the grass. Pomeroy et al. (1972) and others have also noted this seemingly unlikely maximum of phosphorus during the summer months.

The findings of Patriquin (1972) in studying the origin of nitrogen and phosphorus for growth of Thalassia testudinum suggest that significant amounts of phosphate and nearly all nitrogen utilized for growth are obtained from the sediments. The supply of readily available phosphate in the root layer is estimated to be equivalent to that required for three hundred to a thousand days growth while the supply of nitrogen is estimated to be equivalent to that required for five to fifteen days growth. It is believed that the sediments may

buffer the phosphate supply by storing sea water phosphate excreted by _Thalassia_ _testudinum_. The nitrogen is postulated to be derived from fixation by anaerobic bacteria.

Blum (1969) suggested that the _Spartina_ _patens_ marsh acts as a filtering system which removes nutrients when flooded by high spring tides. Total phosphorus concentration was found to decrease during flood tides, but this was as a result of dilution of the phosphorus-rich waters surrounding the _Spartina_ rather than absorption by the mesh of stems.

An additional source of inorganic nitrogen has been determined by Goering and Parker (1972) who found epiphytic algae to be nitrogen fixers. Bacterial nitrogen fixation can also occur in sediments with high reduction potential. Organic materials released by plant roots are utilized by the bacteria which release ammonia needed for plant growth.

Decomposition and Nutrient Regeneration

Spartina _alterniflora_ marshes usually have a photosynthesis to respiration ratio greater than one (Teal, 1962). This excess production is an important source of organic energy to the nearby estuarine waters (Odum and de la Garza, 1967).

Decomposition of organic matter causes a release of soluble organics to the surrounding waters as well as an increase in microbial biomass. The proteinaceous component of marsh plants is converted to organic nitrogen and then undergoes deamination to ammonia. The

ammonia is oxided to nitrite and then to nitrate.

Fenchel (1970) studied the decomposition of detritus derived primarily from Thalassia testudinum. Generally only the outermost or two outermost cell layers were populated by microbial communities. These communities consisted of bacteria, small zooflagellates and diatoms and to a lesser degree, other unicellular algae and ciliates. The bacteria and fungi decomposed the detritus to materials more readily available to the larger plants and animals. In turn, the bacteria were consumed by flagellates and ciliates and the fungi by nematodes. This conversion of low protein marsh grass to high protein microbial mass is an important link in the estuarine food chain (Gosselink and Kirby, 1974).

Aerobic heterotrophic bacteria participate actively in the decomposition of Spartina (Burkholder and Bornside, 1957). Decomposition and utilization of the protein and soluble carbohydrate components of marsh grass proceed rapidly while the crude fiber material (cellulose and lignin of the stems) is decomposed more slowly. Jewell (1971) found a refractory fraction of the plants from 1 - 50%, depending upon species, to resist decomposition over a period of three to six months. The average refractory fraction for healthy plants is 24%. This is approximately half that of algae.

Decomposition of detrital material in situ occurs slowly in winter and more rapidly in spring and summer (Burkholder and Bornside, 1957). Gosselink and Kirby (1974) found conversion efficiency to decrease with increasing particle size. This may be due to the decrease in surface area per unit mass with increasing particle size

which reduces heterotroph access to the particles. This is supported by the studies of Fenchel (1970) which found microbial communities on only the outermost cell layers of particles and accordingly found the number of microorganisms present to be proportional to the surface area.

Jewell (1971) found the regeneration of nitrogen and phosphorus during decomposition to vary from 0% - 100% of the particulate nutrients initially present. The nutrients not regenerated are those remaining in the particulate refractory material. Aquatic plants have the potential to regenerate more nutrients through decomposition than phytoplankton since the plants decay more rapidly and more completely.

Saprophytic fungi have been found to aid in the decomposition process. Gessner, Goos and Sieburth (1972) found Spaerulina pedicellata to colonize in the internodal area of living Spartina alterniflora and to rapidly form a significant biomass during the plant's senescence along with other fungi. This fungal biomass was colonized by bacteria and grazed upon by nematodes and mites.

ATTACHED ALGAE AND ALGAL MATS

Productivity

Optimal light intensity plays an important role in algal productivity. Pomeroy (1959) in studying algae of the Georgia saltmarsh found photosynthesis to occur only with optimal light intensity, this ranging between 350 and 3000 foot candles (depending to some extent

on the major taxonomic group present). With light in the optimal range, algal photosynthesis is temperature dependent. Conover (1958) found these same factors to be of primary importance to benthic marine plants in Massachusetts.

Total daily production of algae in the Georgia saltmarsh does not vary significantly from season to season (Pomeroy, 1959). The gross annual algal production for this saltmarsh is estimated to be 200 gms of C/m^2. Gallagher and Daiber (1974), in studying edaphic algal communities in a Delaware saltmarsh, determined the gross annual production there to be 160 gms of C/m^2 of ash-free dry weight, which is approximately one-third of the angiosperm productivity of that marsh.

In addition to adequate light and temperature, nutrients are also required for algal productivity. Odum, Kuenzler, and Blunt (1958) studied the uptake of phosphorus in marine benthic algae. The rate of uptake was found to be independent of light conditions and to vary between species. Both phosphorus uptake and productivity were proportional to the surface to volume ratio of the algae. Thus, the inherent surface area features of the algae are the determining factors for productivity and phosphorus uptake. Conover (1958) noted that the abundance of benthic plant species followed changes of phosphorus in the spring and nitrogen in the fall (phosphorus concentrations were low in spring; nitrogen concentrations were low in fall). Within the area studied, sections having larger concentrations of nitrate and phosphate were more productive.

Nutrient Cycling

The biomass of algae is immediately available to algae-detritus feeders in the marsh as opposed to the macrophytes which must first die and undergo decomposition (Gallagher and Daiber, 1974). Dead algal cells will undergo decomposition in the same manner as previously described for the macrophytes. However, the algae have a larger refractory fraction than the macrophytes and also decay at a slower rate (Jewell, 1971). Recycling of organic matter from benthic marine plants occurs primarily in situ (Conover, 1966). Armstrong and Hinson (1973) found organic matter to be rapidly produced and released from the marsh following death of emergent plants or algal mats.

The Algal Mat Community

Algal mats have been observed to occur in areas with temperatures ranging from near freezing to 70°C and salinities from less than 1 ppt to greater than 20 ppt (Sorenson and Conover, 1962). The mats in the bays of South Texas are a vibrant green throughout the summer, disappear in winter and reappear in March (Odum, 1967). They are composed of a laminar arrangement of plants and animals. Sorenson and Conover (1962) identified five distinct zones in the algal mats of southern Texas, which was composed mainly of Lyngbya confervoides. The zones are: Zone A, consists of algae with blackened sheaths suggesting that this layer acts as a temperature and light shield for underlying microorganisms; Zone B, is a transition zone having some additive growth; Zone C, is a region of vigorous algal growth; Zone D, consists of remains of microorganisms and an increasing number of

colorless flagellates and bacteria; and Zone E, is an area of decompo-
sition and anaerobic processes. The photosynthetic products of this
laminar arrangement may often remain unconsumed since few consumers
are adapted to contend with the organic matter in the extreme anaerobic
and briny conditions existing before and after deposition (Odum, 1967).
Systematic changes in fatty acids occur throughout the layers of these
algal mats (Parker and Leo, 1965).

An oxidation-reduction potential gradient capable of reacting
to a platinum electrode exists among the ions of the algal mat
(Armstrong and Odum, 1964). This is caused by photosynthesis and
separation of the rising oxygen. The voltage gradient is in the
direction to produce an electrophoresis of negative ions toward the
positive upper surface and this may serve to pump nitrates and phos-
phates to the upper algae. Since nutrients have been found to accum-
ulate on the surface of mats it appears that this does occur (Oppen-
heimer and Ward, 1962). The voltage gradient may also produce an
organization among the blue-green algae which become positioned
in accordance with their charge.

The effect of single doses of phosphate (1 - 100 micromoles/
liter) and nitrate (10 - 100 micromoles/liter) on a marine algal com-
munity have been determined (Abbott, 1967). Consumption of each
nutrient and its effect on productivity is independent of the other.
All nutrients added to the ecosystems were eventually consumed and
excess nutrient levels produced the expected luxuriant growth. A
first-order mechanism for phosphate utilization was associated with
the limiting maximum rate of uptake. The rate of uptake of nitrogen
indicates a more complex reaction sequence with uptake velocity

depressed at high concentrations of dissolved nitrate.

In Cooper's study (1970), microcosm algal production increased when drought conditions were simulated by stopping the inflow of freshwater. However, algal microcosms in more advanced successional stages become nutrient starved and can utilize nutrients rapidly with little noticeable increase in productivity (Armstrong and Hinson, 1973). Nutrient inputs to algal systems are rapidly utilized and converted to additional biomass. Porcella et al. (1970) found that soluble orthophosphate was immediately accumulated by the algal community and was utilized for growth.

SUSPENDED ORGANISMS

The primary producers in saltmarsh ecosystems are the higher plants, the algae in and on the sediments, and phytoplankton found in estuarine waters (Pomeroy, 1959). The higher plants and the phytoplankton are the two major sources of organic material in the estuarine waters (Jewell, 1971).

Phytoplankton utilize inorganic phosphorus converting it to organic phosphorus during photosynthesis. The organic form is re-generated back to the inorganic form via the metabolism of bacteria, phytoplankton, zooplankton and higher organisms in the water (Bruce and Hood, 1959). Phytoplankton may also utilize ammonia, as a source of nitrogen (Zobell, 1946) and are a source of amino acids for the decomposers.

Marine algae have been found to excrete extracellular products to the surrounding water. Four to sixteen percent of photoassimilated carbon is released in this manner by a healthy phytoplankton population (Hellebust, 1965). Evidence has been found that considerable amounts of organic phosphate derivatives and perhaps even inorganic phosphate are excreted (Bruce and Hood, 1959). Diurnal variations of inorganic phosphate in Texas bays are greatest when heavy populations of phytoplankton undergoing rapid growth are present. Within normal light intensities release of extracellular products by phytoplankton is proportional to the amount of carbon fixed. At low light intensities release of these products is relatively greater and at light intensities high enough to inhibit photosynthesis, as much as ninety-five percent of the assimilated carbon may be released as extracellular products (Fogg et al., 1965). In this way, the excreted extracellular products may later serve as a carbon source for phytoplankton and may permit better growth than an inorganic source alone would at low light intensities.

Phosphates are known to be concentrated by algal cells (Round, 1965). This may explain their ability to grow in a medium that becomes devoid of phosphates (Baalsrud, 1967). Nitrogen can also be economized in this way during periods of shortage. When present in low concentrations, the amount of nitrogen apparently determines the rate of growth (Baalsrud, 1967). Pomeroy et al. (1965) found the exchange capacity of the sediments to provide an ample supply of phosphate for phytoplankton during high growth periods when it is needed in larger amounts.

Zooplankton, depending primarily on plant life for nutrition, are also present in estuarine water (Zobell, 1946). They either serve as a food source for larger marine animals and the nutrients they assimilate continue along the food chain or they eventually die and their nutrients are returned to the ecosystem via decay.

SEDIMENTS

Sedimentation is an important process in the saltmarsh. The main components of the sediment are derived from the nearby estuarine environment and upland discharge (Eagleson et al., 1966). The period of maximum accretion occurs in August, except in higher areas of the marsh where accretion is fairly continuous (Ranwell, 1964). The accretion rate in European and Northeastern American coastal marshes was found to be in the range of 0.2 - 1.0 cm/yr. The average rate of sedimentation in Texas bays is 3 ft/century (0.9 cm/yr) (Shepard, 1953). Shoaling in Lavaca Bay occurs at a rate of 0.46 ft/century (0.14 cm/yr) and in East Matagorda Bay it occurs at a rate of 3.5 ft/century (1.1 cm/yr). Lavaca River serves as a sediment source for Lavaca Bay by carrying approximately 160,000 tons of sediment to the Bay exchange (Shepard, 1953). The rate of formation of marsh level high enough for colonization of higher plants in England has been occurring more rapidly than colonization by the plants.

Sediments deposited in estuaries contain organic matter from terrestrial erosion, agricultural runoff, marine debris, and freshwater debris. Ranwell (1964) found sedimentation to supply nutrients at the rate of 800 kg of N/ha-yr and 250 kg of P/ha-yr. The results of the studies of the England saltmarsh suggested that the sediment

supply to marsh zones is derived from lower (more seaward) marsh zones and that these are in turn fed by the bare mud zones to the seaward of them.

The upper layers of saltmarsh sediment are inhabited by bacteria, algae, diatoms, protozoa, and small marine animals. Annelids and other burrowing species will be found in lower layers. Bacterial populations decrease from the surface downward, the decrease occurring most rapidly in the uppermost few centimeters (Zobell, 1946). Bacteria are of importance in the decomposition of organic detrital material in which nutrients are regenerated to the saltmarsh. Products of decomposition lead to nutritionally rich sediments. The bacterial biomass can be assimilated by filter-feeding and mud-eating animals. The burrowing species can cause mixing and translocation of the sediments. Chemical conditions are also affected by the micro-organisms in the sediments. Seasonal cycles in organic productivity and meteorological conditions cause seasonal changes in the species inhabiting the bottom in shallow waters (Zobell, 1946).

Nutrient Exchange

The exchange of nutrients between the sediments and the over-lying water column occurs as a result of complex interactions of biological, physical, and chemical processes. Microbial processes effect the nutrient exchange occurring at the sediment-water interface directly through assimilation and release as well as indirectly by alteration of pH and the oxidation-reduction status of the sediments, and the production of gas. Lee (1970) regards hydrodynamic effects such as currents to be rate-controlling since they alter the concentration

gradient and cause exchanges to occur in order for the sediment-
water interface to return to equilibrium. Nutrient exchange across
intertidal sediment surfaces may be further enhanced by the vertical
movement of the water as it evaporates during low tide and is re-
placed during high tide (Pomeroy et al., 1965). Actual quantities
of carbon, nitrogen and phosphorus retained in the sediments are in-
fluenced by the oxidative capacity of the water (Serruya, 1971).

Phosphorus

Phosphorus in the sediments may be in several forms: calcium
phosphate, organic phosphate, orthophosphate dissolved in the
interstitial water, aluminum and iron phosphate compounds or as
phosphate adsorbed on silicates. Phosphorus in organic forms is
released from the sediments through dephosphorylation by phosphatase
enzymes of various microorganisms (Fillos and Swanson, 1975).
During the degradation of organic matter, organic and inorganic
acids are formed which may dissolve inorganic phosphate compounds.
The phosphorus may be released to the overlying water or retained by
the sediments.

Porcella et al. (1970) have conducted studies of the biological
effects on sediment-water nutrient exchange. The sediments served
as the phosphorus source for algae and the amount of growth was
found to vary with the amount of phosphorus in the sediments. More
productive systems were generally those with greater phosphorus
concentrations in the sediments.

Hayes and Phillips (1958) in studying phosphorus exchange between lake sediments and water found their results to suggest that in small, shallow lakes phosphorus exchange is dominated by the growth and bacterial decomposition of rooted aquatic plants. Both Zostera marina (eelgrass) and Spartina alterniflora have been found to absorb excess phosphorus from sediments and release them to surrounding waters (McRoy, Barsdate, and Nebest, 1972; Reimold, 1972). Pomeroy et al. (1972) found Spartina to remove all or most of its phosphorus from subsurface sediments.

Phosphate exchange combines a sorption reaction and a biologically controlled exchange (Pomeroy et al., 1965). The sorption reaction consists of a rapidly occurring surface sorption and a slower, secondary combination of phosphate with the clay lattice. The biological process occurred at the same rate as the faster sorption process indicating an exchange across cell membranes rather than assimilation. The concentration gradient of phosphorus at the sediment-water interface is the driving force of the sorption process (Carritt, 1954).

Gooch (1968) proposed a mechanism for the seasonal variation of inorganic phosphate (high summer concentrations and low winter concentrations). Water conditions in autumn (pH greater than 7.0, minimal hydrogen sulfide production) cause the formation of ferric phosphate which removes dissolved phosphorus from the water and keeps it bound in the compound throughout the winter. As the pH decreases in spring, ferric ion is reduced to ferrous, sulfide production increases and pyrites are formed, all of which lead to the release of phosphorus from the precipitated to the dissolved form. As sulfide

production increases during the summer months the phosphorus release increases. Serruya (1971) found a good correlation between phosphorus and iron in the sediments of Lake Kinneret. Precipitation has been found to contribute significantly to the nutrient concentration of saltwater marshes and may be a contributing factor to high summer concentrations (Reimold and Daiber, 1970) since higher salinities and temperatures in summer affect the solubility product. The high summer concentrations may also be associated with aerial application of insecticides and agricultural utilization.

The cycling of phosphorus in estuarine waters of Georgia is primarily controlled by metabolic processes and secondarily by physical-chemical processes (Pomeroy et al., 1972). The sediments are able to supply sufficient phosphorus to phytoplankton and benthic plants during periods of high productivity or temporarily increased flushing (Pomeroy et al., 1965).

Nitrogen

Nitrogen is present in sediments mainly in organic forms but may also be present as ammonia-nitrogen, nitrate-nitrogen, or nitrite-nitrogen. The concentration of each of the species that is present is dependent upon rates of immobilization, mineralization, nitrification, and denitrification. Ammonium and organic nitrogen compounds are known to be readily sorbed by clay and other inorganic colloids. Shapiro (1970) and Ryther and Dunstan (1971) suggest that nitrogen in coastal marine waters is the critical limiting factor to algal growth and eutrophication.

Rapid turnover rates of ^{32}P and ^{15}N indicate that assimilation and regeneration by the plankton and protozoans occurs rapidly. Although bacteria are normally considered to be of importance in releasing nutrients from organic matter, studies by Johannes (1968) have indicated that aquatic animals may dominate the process. Due to the high metabolic rates of herbivorous zooplankton, they are able to consume and release back to the water an amount of nutrients several times greater than their body weight. Autolysis and solubilization are also rapid mechanisms of nutrient release (Fenchel, 1970).

Under aerobic conditions a higher rate of nitrogen mineralization will occur than under anaerobic conditions (Jewell, 1971). Increase in temperature will increase the rates of regeneration, turnover, and assimilation.

The rate of nitrification in sediment-water systems doubles with each 10°C increase in temperature (from 0°C to 40°C). Most nitrification is attributed to autotrophs (Chen et al., 1972a). Nitrate was found to be released to overlying water in appreciable amounts only in well oxidized, stirred situations such as those which may occur in shallow water. Nitrification has been found to occur in surface layers of lake sediment with subsequent denitrification occurring in the reduced subsurface zone of the sediments. Denitrification in marine sediments varies widely and appears to be inversely related to the carbon to phosphorus ratio of the sediment (Chamroux, 1965).

Nitrogen fixation rates in lake and estuarine sediments are normally low and fixation may be only of minor importance in these environments (Brezonik, 1971). However, in studying the source of

nitrogen for growth of _Thalassla testudinum_, Patriquin (1972) postu-
lated that nitrogen in the sediments is derived primarily from fixation
by anaerobic bacteria.

SALTMARSHES

In studying a saltmarsh of Delaware, Reimold and Daiber (1970)
found a linear relationship to exist between salinity and total and
inorganic phosphorus. Phosphorus concentrations are high compared
to other saltmarshes on the east coast and are attributed to residence
time, turnover rates, and abundant supply of the nutrient. The phos-
phorus concentration reaches a maximum in summer and a minimum in
winter in this area.

The productivity of a saltmarsh in Georgia was determined and
found to be high. Forty-five percent of the net production was
exported to surrounding water by the tides. In this manner the salt-
marsh supports an abundance of life found beyond its immediate
boundaries (Teal, 1962). Pomeroy et al. (1972) also studied marshes
in Georgia. Phosphorus was never found to be a limiting factor of
productivity in these studies. Respiratory processes were found to
remain constant throughout the year. (Higher phytoplankton produc-
tion in spring and summer is balanced by higher production of inter-
tidal microflora and larger algae in winter.)

Maurer and Parker (1972) studied the concentration of dissolved
organic carbon in the coastal waters of Texas (both estuaries and the
Gulf near the coast overlying the continental shelf). The concentra-
tion of dissolved organic carbon was determined at a point toward

north Lavaca Bay and found to be 4.9 mg/l and at a point in south
Lavaca Bay it was 4.6 mg/l. Dissolved organic carbon concentrations
in Matagorda Bay (to the south of and connected with Lavaca Bay)
ranged from 3.6 mg/l to 4.2 mg/l. As with all other Texas bays these
values exceed those of the Gulf waters (1.0 - 3.7 mg/l DOC) indicating
the high productivity of the estuarine area. Wilson (1962) studied
total organic carbon in Texas bays and found it to be five to ten times
that in the Gulf. These values are higher than those of Maurer and
Parker due to the high amount of particulate matter (total organic carbon
is the sum of particulate and dissolved organic matter) in the bay
waters. The samples in this study were taken during a drought so
evaporation may have increased the dissolved organic carbon content
(Maurer and Parker, 1972).

It appears that either rapid cycling of inorganic phosphorus or
a dynamic exchange with sediment and suspended materials exists
to provide sufficient phosphorus for the observed productivity (Bruce
and Hood, 1959). Inorganic phosphate increases following sunset
and decreases beginning with sunrise indicating the existence of a
relationship between the inorganic phosphate variation and photo-
synthetic activity. This appears to be the case since largest diurnal
fluctuations were found to occur in areas of heavy phytoplankton popu-
lations undergoing rapid growth. The turnover rate for phosphorus
in Texas bays was determined to be ten to twenty days. Pomeroy
(1963) found the turnover rate of phosphorus to decrease in periods
of darkness which also suggests the importance of photosynthetic
organisms in turnover.

Initial studies of cycling of nutrients in saltwater marshes of Lavaca Bay were done by Armstrong et al. (1975). In field studies in July (emergent vegetation was partially submerged during the flooding period and dry towards the end of the ebbing period) organic nitrogen and total organic carbon were found to be exported from the marsh area while small amounts of inorganic nitrogen and larger amounts of orthophosphorus were taken up by the marsh. Additional field studies were done in August at which time flow was confined to the main channels and larger depressions in the area, leaving the marsh almost dry. All forms of nitrogen, phosphorus, and carbon were exported from the marsh with the export of organic materials being greater than inorganic. Marsh reactor studies were also done on portions of the marsh which had been removed (both algal mat and emergent plant communities). Total organic carbon and organic nitrogen were exported from the reactors. The inorganic nitrogen species (ammonia, nitrate, nitrite) and total and orthophosphorus exhibited a net loss to both plant communities.

CHAPTER 3

EXPERIMENTAL PROCEDURES

INTRODUCTION

This chapter describes the laboratory apparatus and work done as well as the methods of analyzing the resulting data. First, the area of Lavaca Bay from which marsh samples were obtained and the acquisition of these samples are described; second, the laboratory microcosms and marsh simulation are described; third, the sampling methods and schedule are given; and fourth, the methods used in analyzing the data are explained.

THE LAVACA BAY SALTMARSH AREA

A series of bays are located along the Texas Coast. The transition from these brackish water bays to the land freshwater flows occurs through areas of marsh formed by deposition of sediment. The water in these areas is normally shallow and brackish and vegetation abounds. An area of the Lavaca Bay Marsh was utilized in this study. It is located 9.5 miles NNE of the City of Port Lavaca. Samples of the marsh system were removed from a peninsular area (about two miles long) located between Swan Lake and Lavaca River which both flow into Lavaca Bay. The location of the sampling site in relation to Swan Lake can be seen in Figure 1 (as the core and reactor sites).

26

FIG. 1. LOCATION OF LAVACA BAY MARSH SAMPLING SITE
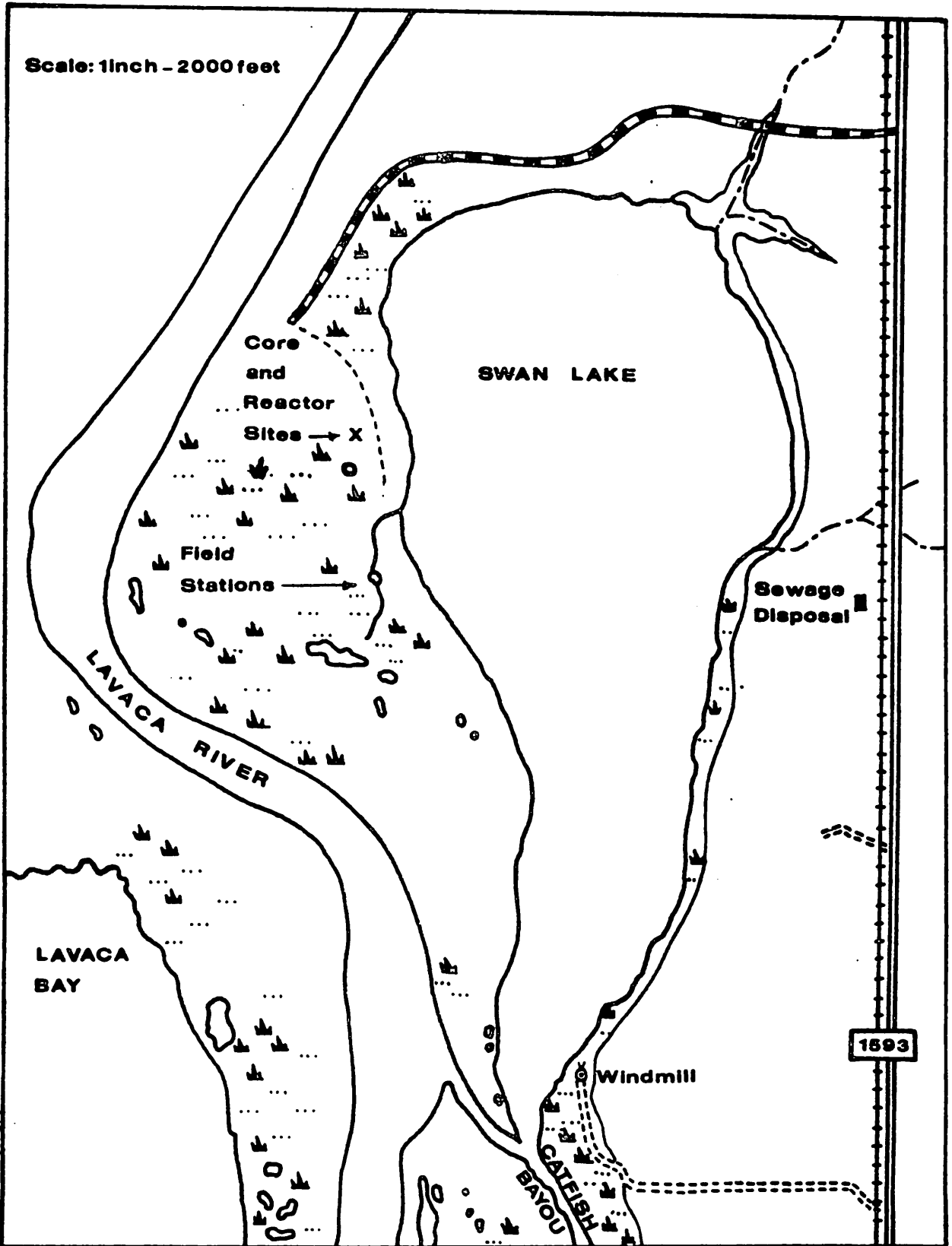
The saltmarsh area was visited for procurement of portions of the marsh system for use in the laboratory microcosms in mid-March, 1975. At this time the area was covered with approximately eight to eleven inches of water and marsh grasses present were a healthy green. The algal mat had not yet formed but algae were present both floating on the water and resting on the sediments.

During summer, 1974 (Armstrong et al., 1975) dissolved oxygen in this area ranged from 0 - 12 mg/l; ammonia nitrogen from 0.1 - 1.7 mg/l; organic nitrogen from 0.5 - 3.8 mg/l; nitrate nitrogen from 0.03 - 0.06 mg/l; nitrite nitrogen from 0.03 - 0.06 mg/l (although same range as nitrate, nitrite values always exceeded nitrate values); orthophosphate from 0.01 - 0.26 mg/l; total phosphate from 0.05 - 0.7 mg/l; and TOC from 3 - 63 mg/l.

Acquisition of Saltmarsh Plants and Sediments

Plastic pails (Rubbermaid - 13.5 inch diameter, 15.5 inch depth), which were used as containers for the microcosms in the laboratory, were taken to the marsh area and portions of the marsh system were placed directly in them. Marsh grasses and their roots were removed with a shovel and placed in the pails on top of a few inches of sediment (to allow for additional root extension). The total sediment depth in these pails was about eight inches. Four pails were filled in this manner with representative portions of the marsh grasses and their underlying sediments. Although algal mats had not yet formed, samples of the algae present were placed in two pails over a layer of sediment about four inches deep. (Algal mats formed from this algae in the laboratory.)

Two to four inches of water from the marsh were placed in each pail to maintain the partially inundated conditions present in the field during transport back to the laboratory. The microcosms were taken to the laboratory late in the day, placed under lights, and maintained in this way for three days. After this time, a constant flow of saline water containing low nutrient concentrations was pumped through the reactors at a low flow rate. (The concentrations described as low are: 0.2 mg/l of NH_3-N, <0.1 mg/l of Org-N, <0.02 mg/l of NO_3-N, <0.01 mg/l of NO_2-N, 0.05 mg/l of Ortho-PO_4, and 0.05 mg/l of Total PO_4.) This was continued for three and a half weeks in order to allow the plants to become acclimated to the laboratory conditions.

LABORATORY SIMULATION OF THE SALTMARSH

The Marsh Microcosms

Influent water for each microcosm was kept in an individual five gallon carboy. The water was pumped from the carboy through plastic tubing by a Cole Parmer pump and entered the microcosm above the water surface. Water drained from the microcosm through a constant water level glass-tubing siphon. The influent and effluent points were opposite each other to minimize short-circuiting. Each microcosm was continuously stirred by a T-Line Laboratory Stirrer* to simulate the stirring of water in the saltmarsh by the wind and tides. A diagram of this apparatus is presented in Figure 2. The microcosms were numbered from one to six and the marsh or algal system and

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* Talboys Engineering Corp., Emerson, N. J.
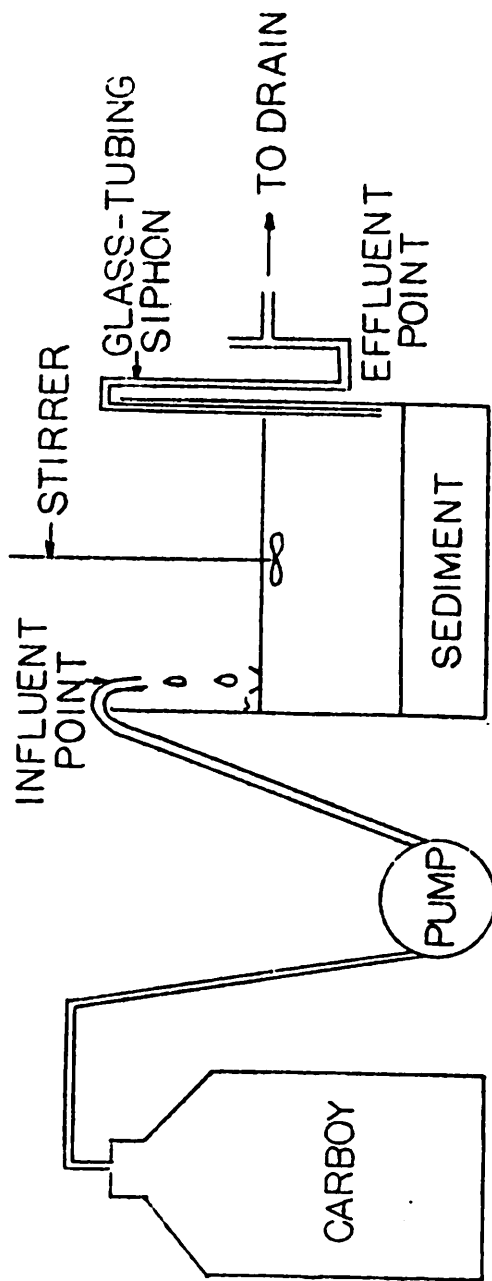
FIG.2. MICROCOSM APPARATUS

nutrient conditions maintained in each are described in Table 1.

Lighting

Lights were mounted in a rectangular frame which was placed over the six microcosms. Four Ken Rad 25 watt incandescent bulbs were in the center along the length of the frame. To either side were four 40 watt daylight Ken Rad fluorescent bulbs, also placed lengthwise. By using both incandescent and fluorescent lights, the plants received wavelengths of light in both the near infra red and blues.

The lights remained on from 0800 to 2000 at which time the microcosms were covered with an opaque material to prevent the reception of any further light by the plants. To facilitate the drying process (a period of drying was simulated during the study) the incandescent bulbs were replaced by 250 watt Sylvania infrared heat bulbs for the initial thirteen days of the drying period. A listing of the intensity of light reaching each microcosm from the incandescent and fluorescent bulbs as well as from the heat and fluorescent bulbs is given in Table 2. According to Pomeroy (1959) the optimum light intensity for algae of the Georgia saltmarsh ranged from 350 - 3000 foot candles. Thus, there is a possibility (refer to Table 2) that light intensity was a limiting factor to the productivity of algae.

Influent Water

Instant Ocean Synthetic Sea Salts* were mixed with distilled

* Aquarium Systems, Inc., Eastlake, Ohio

TABLE 1

DESCRIPTION OF MICROCOSMS

Microcosm	Primary Flora	Influent Nutrient Level
1	marsh grass	low
2	marsh grass	additional nutrients
3	marsh grass (sediments covered by paraffin layer)	low
4	marsh grass (sediments covered by paraffin layer)	additional nutrients
5	algal mat	low
6	algal mat	additional nutrients

TABLE 2

LIGHT INTENSITIES IN THE MICROCOSMS

Microcosm	Incandescent and Fluorescent Lights			Heat and Fluorescent
	At Sediment Surface (foot-candles)	1" Above Sediment (foot-candles)	4" Above Sediment (foot-candles)	At Sediment Surface (foot-candles)
1	320	340	440	770
2	320	345	420	770
3	280	300	430	900
4	260	290	400	850
5	150	160	230	580
6	180	190	260	610

water to attain a salinity of 5 ppt. The chemical analysis of the Instant Ocean water is given in Table 3 and the laboratory analysis of the amounts of nitrogen and phosphorus present in the distilled water is given in Table 4. The Instant Ocean Water was mixed in a one hundred fifty gallon container and the five gallon carboys were filled from it. Mixing this large quantity provided a consistent salinity throughout the study.

When the Instant Ocean water was transferred to the individual carboys, the trace element solution was added to all of them, and additional nitrogen and phosphorus were added to the carboys supplying microcosms 2, 4, and 6. Ammonium chloride was added to provide an additional 5 mg/l of nitrogen and potassium phosphate monobasic provided an additional 2 mg/l of phosphorus.

REACTOR HYDRAULICS

Water Level

Initially, the level of water in the microcosms was set at four inches above the sediment surface in Microcosms 1, 2, 5, and 6 and at four inches above the paraffin surface in Microcosms 3 and 4. (After the acclimation period the sediments in Microcosms 3 and 4 were covered with a layer of paraffin which sealed the sediments from the overlying water column preventing nutrient exchange between the sediments and water. Nutrient exchanges occurring in these micro-cosms then must take place between the plants, suspended organisms and water column with the exception of the possible transport of nutrients from sediments by the roots of the plants). Over a period

TABLE 3

INSTANT OCEAN SYNTHETIC SEA SALTS SOLUTION

Element	Final Concentration (ppm)
Cl	18400
Na	10200
SO_4	2500
Mg	1200
K	370
Ca	370
HCO_3	140
H_3BO_3	25
Br	20
Sr	8
SiO_3	3
PO_4	1
Mn	1
MoO_4	0.7
S_2O_3	0.4
Li	0.2
*Rb	0.100
*EDTA	0.050
*Al	0.040
*K	0.020
*Zn	0.020
*V	0.020
*Fe	0.010
*Co	0.010
*Cu	0.003
*SO_4	0.298
*I	0.073
*Cl	0.050

* Present in trace elements solution.

TABLE 4

NUTRIENT CONTENT OF DISTILLED WATER
USED FOR DILUTION

Nutrient	Concentration (mg/l)
NH_4-N	0.2
NO_3-N	<0.02
NO_2-N	<0.01
Ortho-PO_4-P	0.02

of three weeks the water level was gradually lowered until no water remained, at which time the period of drying was begun. After the drying period of five weeks, the microcosms were filled to the initial four-inch water level and nutrient exchange was monitored for the remaining two weeks. (See Table 5 for the schedule of the study.) Thus, the nutrient exchange rate under conditions of partial inundation was studied as well as the effects of summer drying.

Influent Flow

Constant flow conditions were maintained throughout the study. The flow rate was set to provide a twelve-hour residence time and, therefore, was changed in accordance with changes in the water level. It was necessary to change the tubing in the pump heads frequently to avoid fatigue of the tubing which would cause variations in the flow rate. The flow rate was checked regularly and maintained within 1.5 ml/min of the desired flow rate at high flow (13 ml/min) and within 1 ml/min at medium flow (3 ml/min). Deviation of the flow rate was not determined at the low water level since no analyses could be done at that time.

PRODUCTIVITY OF MICROCOSMS

The microcosms fluorished throughout the study. It was necessary to trim the emergent vegetation periodically as it approached the level of the lights in its growth. Snails were present in all the microcosms but were apparently most abundant in the algal mat microcosms. Algal growth appeared to be more intense in microcosms which received water enriched with additional nutrients than in those

TABLE 5

EXPERIMENTAL SCHEDULE

Week	Water Level (in.)	Sampling Frequency	Sampling Time
1	4	Daily	1200
2	1	Twice Daily	0800 2000
3	0.25 - 0.5	None	____
4 - 8	0	None	____
9 - 10	4	Daily	1200

receiving low concentrations of nutrients. During the period of drying much of the emergent vegetation died and the algal mat was reduced to a papery crust. When reinundated to the initial water level, all of the microcosms recovered and returned to their original states of productivity. New shoots of marsh grass appeared periodically and grew rapidly, normally reaching the height of the original plants within about a week. Algal mats also began to regenerate and were approaching their former level of productivity by the second week.

SAMPLING

Nutrients

Water samples for nutrient analyses were taken in accordance with the schedule in Table 5. (Samples were taken in random order.) Thus, samples were taken during a two-week period before drying and a two-week period after drying. They were taken both in the morning and evening during the second week of the study to determine whether any significant diurnal variation in nutrient exchange occurred. Samples were taken from each microcosm as well as from one influent water source with low nutrient concentrations and one with additional nutrients to permit the calculation of nutrient mass balances. The samples were analyzed for organic nitrogen, ammonia, nitrate, nitrite, orthophosphate and total phosphate at the Texas State Health Laboratory and for total organic carbon (TOC) at the Center for Research in Water Resources, Balcones Research Center. The samples were preserved by adding concentrated sulfuric acid to the nitrogen samples and chloroform to the phosphorus samples and storing the samples at $4^{\circ}C$ (as specified in Standard Methods, 1971) until they were

transported to the Texas State Health Laboratory for analysis. The samples taken for analysis of TOC were frozen until this analysis was performed.

Additional Parameters

When nutrient samples were taken, the pH of each microcosm and the influent waters was determined using a Beckman pH meter. Temperature of the water in the microcosms was determined periodically throughout the study and was found to remain almost constant (approximately 23°C). Dissolved oxygen measurements were taken in the morning and evening for several consecutive days using a YSI dissolved oxygen probe. This data did not show the expected diurnal effects and portrayed no definite pattern. The fact that so many of the components of the microcosms affect the dissolved oxygen concentration makes it difficult at best to determine what occurred.

ANALYSIS OF DATA

The overall nutrient exchange in the microcosms is described by the following equation:

$$\frac{dS}{dt} = \frac{Q}{V} (S_o - S) - f(sediments) - f(plants) - f(pail) \qquad (1)$$

where, $\qquad \frac{dS}{dt}$ = rate of change of nutrient concentration with time,

$$\frac{Q}{V}(S_o - S) = \text{rate of change of nutrient concentration}$$

$$\text{due to influent gains and effluent losses,}$$

$$f(\text{sediments}) = \text{nutrient exchange with sediments,}$$

$$f(\text{plants}) = \text{nutrient exchange with plants,}$$

$$f(\text{pail}) = \text{nutrient exchange with pail surface.}$$

If no sediments or plants are present:

$$\frac{dS}{dt} = \frac{Q}{V}(S_o - S) - f(\text{pail}) \tag{2}$$

By eliminating the plants and sediments, that is, by analyzing samples of water from pails receiving a constant flow of Instant Ocean water, f(pail) was determined. This was done with Instant Ocean water containing both low nutrient concentrations and additional nutrients. Since two of the reactors contained paraffin layers which were in contact with the water, f(pail) was determined for Instant Ocean water (both low nutrient concentrations and additional nutrients) overlying a paraffin layer.

The pail receiving Instant Ocean water with low nutrient concentrations took up slight amounts of ammonia nitrogen and phosphate for three days after which no further uptake was noted. When spiked Instant Ocean water was added to this system no additional nutrient uptake was observed despite the increased concentration gradient. The pail with paraffin receiving Instant Ocean water with low nutrient

concentrations also took up slight amounts of ammonia nitrogen and phosphate for three days. When spiked Instant Ocean water was added to this system, further uptake of ammonia nitrogen and phosphate occurred. This was in small amounts and after three days no further uptake occurred. Essentially all uptake of nutrients by the pails or by the pails and paraffin occurred within five to six days. Since all the microcosms received a constant flow of Instant Ocean water for three and a half weeks prior to the beginning of sampling, it can be assumed that the pails or pails and paraffin had already taken up as much of the nutrients as they could. Thus, the term, f(pails), was essentially zero during the experimental work and Equation (1) becomes:

$$\frac{dS}{dt} = \frac{Q}{V} (S_o - S) - f(\text{sediments}) - f(\text{plants}) \tag{3}$$

Since $(S_o - S)$ indicates the net change in nutrient concentration based on influent and effluent concentrations, the value of this term also represents the net change in nutrients due to sediment and plant exchange. This value was plotted vs. time for each nutrient species in each microcosm throughout the study. From these graphs, trends in net exchange can be determined prior to and after the drying period, and the nutrient exchange of the microcosms can be compared.

Rather than calculate the exchange rate per unit volume of water $(\frac{Q}{V} (S_o-S))$, which would require a knowledge of the depth of water overlying a marsh in order to compare these values with other marsh areas, the mass of nutrients exchanged per unit area of the marsh was calculated. That is, Equation (3) was multiplied by the depth of water, H, yielding:

$$H \frac{ds}{dt} = \frac{Q}{A} (S_o - S) - H f (sed) - H f (plants) \qquad (4)$$

Rearranging this becomes:

$$\frac{Q}{A} (S_o - S) = H \frac{ds}{dt} + f(sediments) + f(plants) \qquad (5)$$

By integrating the result of calculations of the left-hand term of Equation (5) (plotting the mass of nutrients absorbed or released per unit area cumulatively vs. time), the amount of nutrients exchanged during the study could be determined. The slope of this plot will give the rate of exchange per unit area. As with the plotting of $(S_o - S)$ vs. time, the exchange of the microcosms can be compared to one another and by doing so the comparative magnitudes of the primary sources and sinks determined.

Thus, integrating Equation (5) by a modified, simple numerical procedure:

$$\Sigma \frac{1}{A} \frac{\Delta v}{\Delta t} (S_o - S) \Delta t = H [\Sigma \frac{\Delta s}{\Delta t} \Delta t + \Sigma f(sed) \Delta t + \Sigma f (pl) \Delta t] \qquad (6)$$

Examination of the raw data reveals the fact that $\frac{\Delta s}{\Delta t}$ is essentially zero after an initial period of adjustment of the microcosms to new water level conditions (as occurs at the beginning of week one, week two, and after the period of drying). This initial period of adjustment occurred within about two days during weeks one and two and within a little longer time interval after the drying period. Thus, $\frac{\Delta s}{\Delta t}$ was zero during a majority of the study and the microcosms were at steady state. At steady state, the final equation describing the

nutrient exchange in the microcosms is:

$$\Sigma \frac{1}{A} \frac{\Delta v}{\Delta t} (S_o - S)\Delta t = H [\Sigma f(sed)\Delta t + \Sigma f(plants)\Delta t] \qquad (7)$$

In the case of Microcosms 3 and 4, where sediments are sealed from the overlying water by the paraffin layer, essentially eliminating exchange between sediments and water, Equation (7) becomes:

$$\Sigma \frac{1}{A} \frac{\Delta v}{\Delta t} (S_o - S)\Delta t = H \Sigma f(plants)\Delta t \qquad (8)$$

CHAPTER 4
RESULTS

INTRODUCTION

The results of the laboratory studies are presented below. Results of the marsh grass microcosms are presented first followed by those of the algal mat microcosms. Nutrient exchange (mg/l) throughout the study and exchange of nutrient per unit area throughout the study have been plotted for each nutrient in each microcosm. The slope of the plot of nutrient exchange per unit area vs. time gives the exchange rate of the nutrients. The first section of this chapter describes the exchange of nutrients (mg/l) in each microcosm throughout the study; the second, describes the rate of exchange and the cumulative mass of nutrients exchanged by each microcosm; the third, discusses the rates of exchange; the fourth, gives information on the additional parameters which were measured; and the final section, summarizes the exchange of nutrients by the microcosms.

MARSH GRASS MICROCOSMS

Marsh Grass - Sediment Community : Microcosm 1

This community contained marsh grass and sediments along with the microorganisms present when the system was removed from the Lavaca Bay saltmarsh in March.

Ammonia-nitrogen was taken up (0.0 - 0.2 mg/l) during the first week and released during the second (0.0 - 0.4 mg/l) (see Figure 3). After the period of drying, larger amounts (~0.3 mg/l) were released for eight days and after this time release remained between 0.0 and 0.3 mg/l. Organic nitrogen was released throughout the first two weeks (0.0 - 0.5 mg/l) (see Figure 3). Following the drying period concentrations greater than 0.5 mg/l were released for one and a half days with release remaining less than that for the remainder of the after drying period. Low amounts of nitrate and nitrite were released during the first two weeks (see Figure 4). Nitrite was released at a higher rate for twelve hours after the end of the drying period and nitrate for twenty-four hours. Release of nitrite and nitrate began to increase slightly at the end of the recovery period. Overall, the net nitrogen exchange was a release to the water (Figure 3). This was at a constant rate by day 4, with a higher rate occurring for the first ten days of reinundation after drying.

Orthophosphate and total phosphate were released throughout the first two weeks (0.0 - 0.2 mg/l) (see Figure 5). The orthophosphate concentrations paralleled total phosphate and comprised a fairly consistent portion of it. After the drying period larger amounts were released for twenty-four hours, and by day 65 slight amounts of phosphorus were taken up by the ecosystem and this continued throughout the remainder of the two weeks following the drying period.

From 1 - 6 mg/l of TOC were released during the second week*

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* No values are given for TOC in the first week for any reactor due to analytical difficulties.
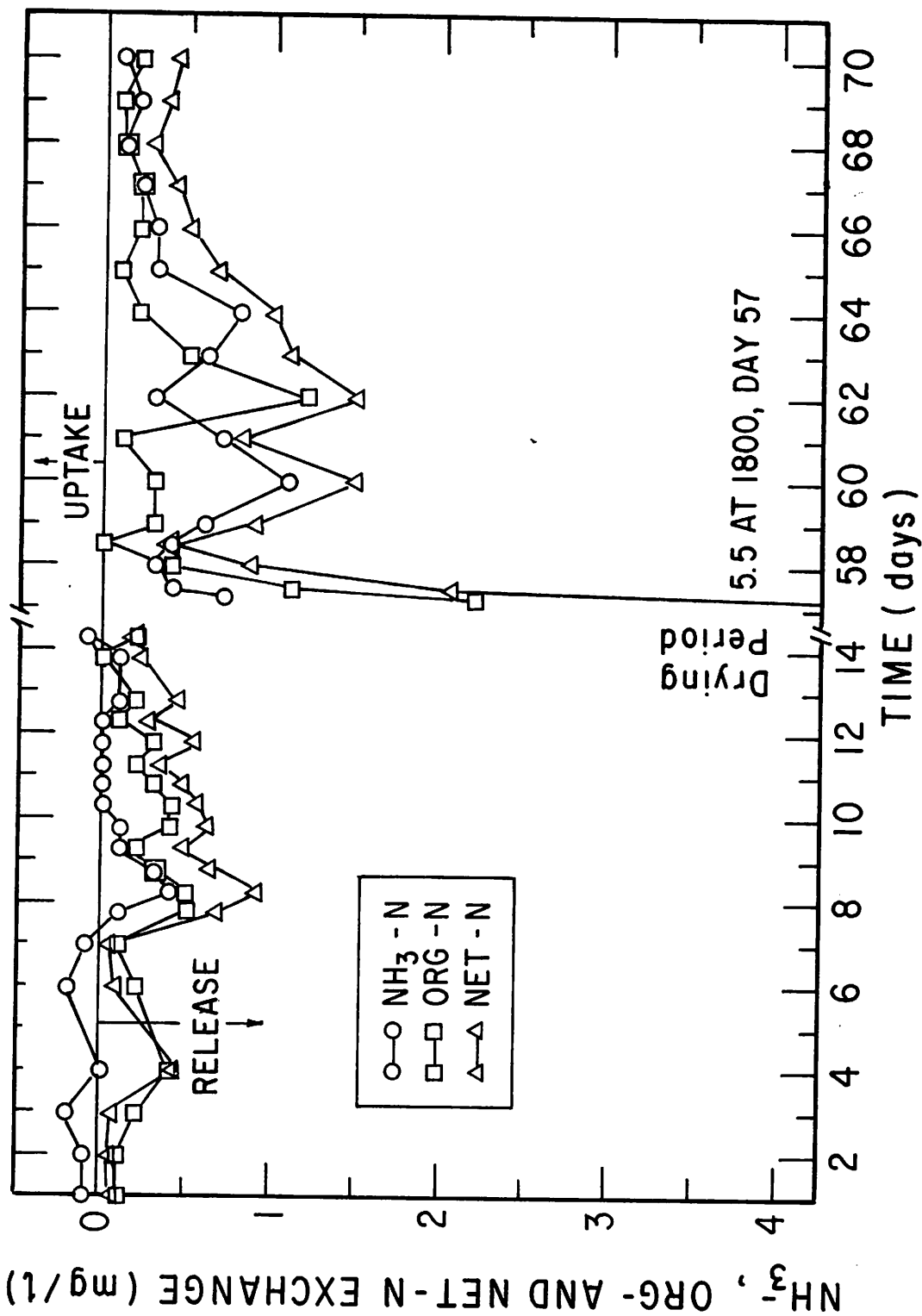
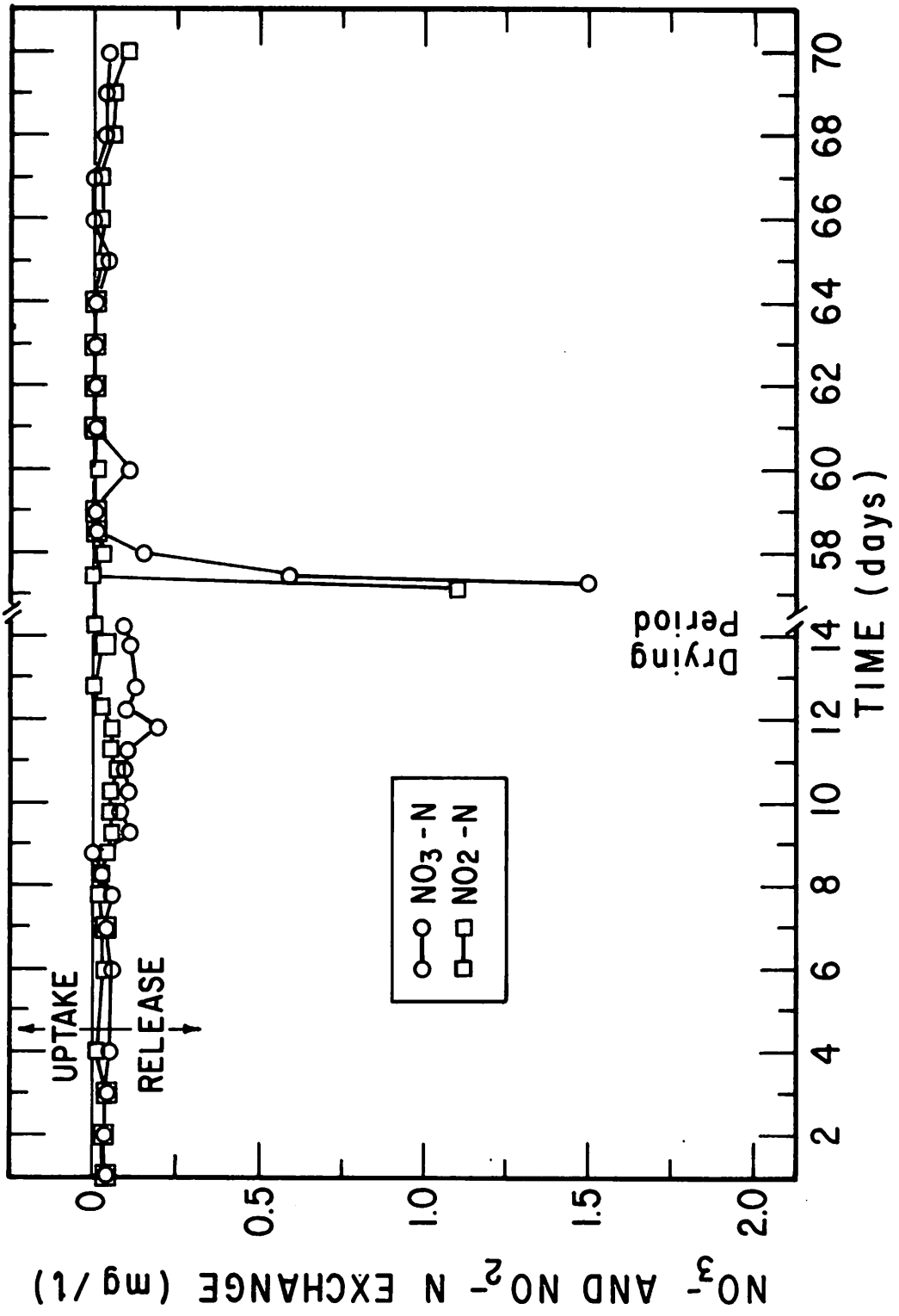FIG. 3. NITROGEN EXCHANGE IN MICROCOSM 1 (MARSH GRASS-SEDIMENT – UNSPIKED)

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FIG. 4. NITROGEN EXCHANGE IN MICROCOSM 1 (MARSH GRASS-SEDIMENT – UNSPIKED)
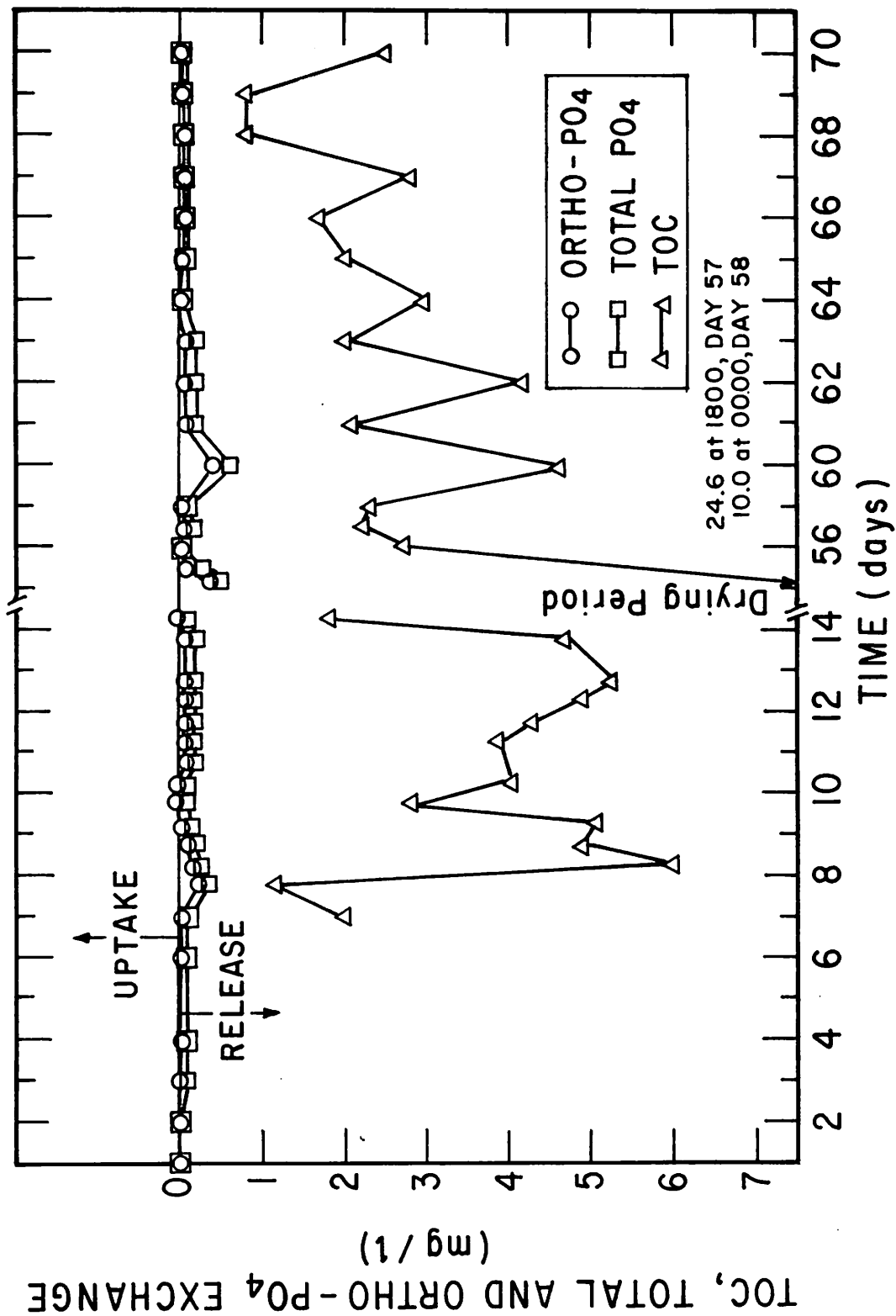
FIG. 5. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 1
(MARSH GRASS-SEDIMENT – UNSPIKED)

(Figure 5). Following the drying period, greater than 5 mg/l were released for twelve hours, and release remained between 2 and 5 mg/l for the rest of the two week period after drying.

Marsh Grass - Sediment Community : Microcosm 2

This microcosm contained the same components as the first, the only difference being that influent water in this case, contained additional amounts of nitrogen (additional 5 mg/l NH_3) and phosphorus (additional 2 mg/l PO_4).

Ammonia nitrogen was taken up during the first two weeks (Figure 6). From 0.0 to 2.2 mg/l were taken up during the first week and this increased to as much as 4.9 mg/l the second week. After drying, ammonia was released for a seven-day period after which it was again taken up. By the end of this two-week recovery period, the amount of ammonia being taken up was in the same range as that taken up previous to the drying period. Organic nitrogen was intermittently released and taken up during the first two weeks (Figure 6). There was a high release of organic nitrogen for two days after the drying period followed by a continued release at a lower rate. Low concentrations of nitrate and nitrite were released during the first week, followed by an increasing release in the second week (Figure 7). After drying, nitrate was released for twenty-four hours and no further release of nitrate or nitrite occurred until the beginning of the second week after which time the release increased. (Increasing release of nitrite and nitrate coincided with increasing uptake of ammonia.) The net exchange of nitrogen was one of uptake prior to drying, release for a nine-day period after drying and a return to net
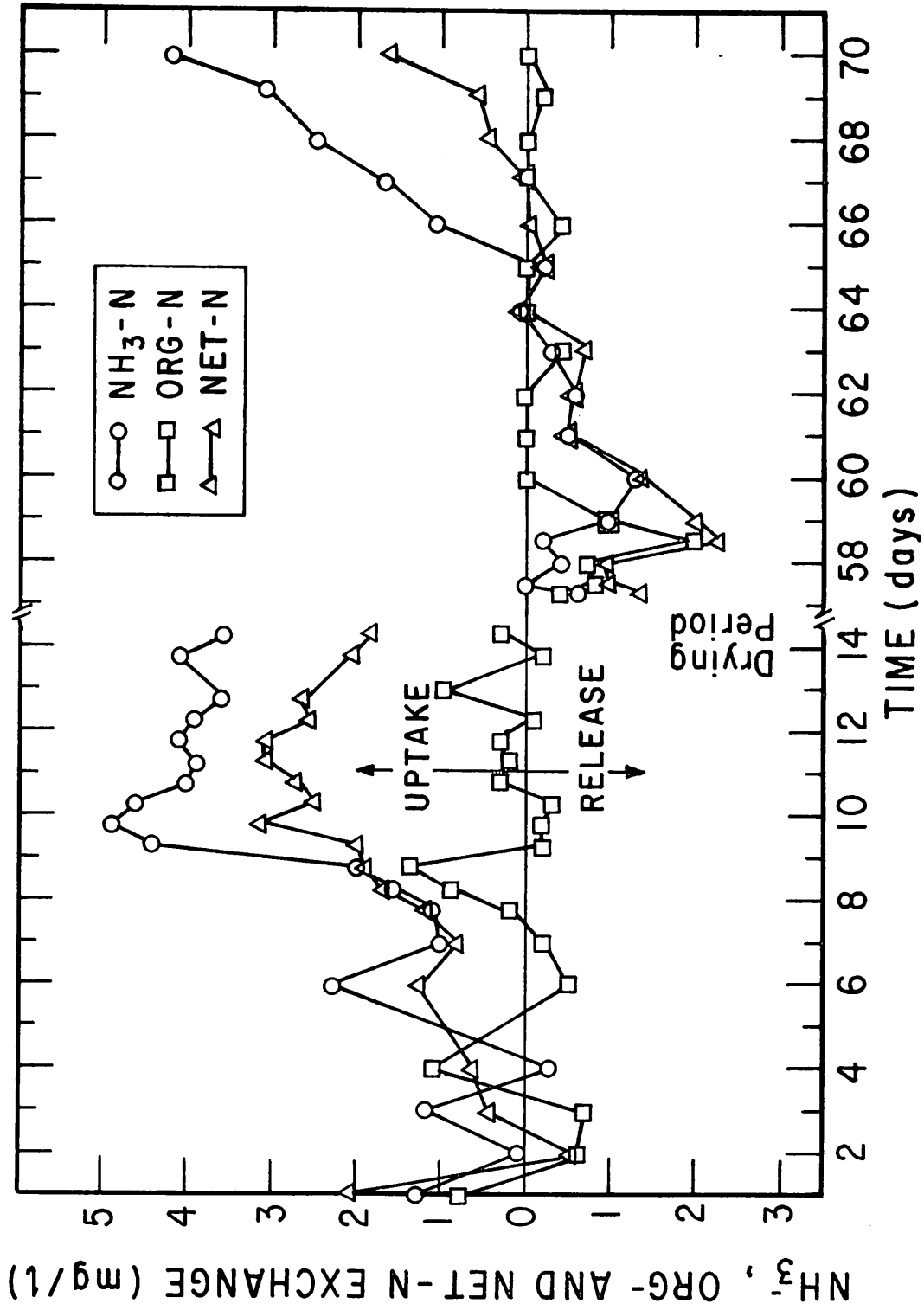
FIG. 6. NITROGEN EXCHANGE IN MICROCOSM 2 (MARSH GRASS-SEDIMENT - SPIKED)
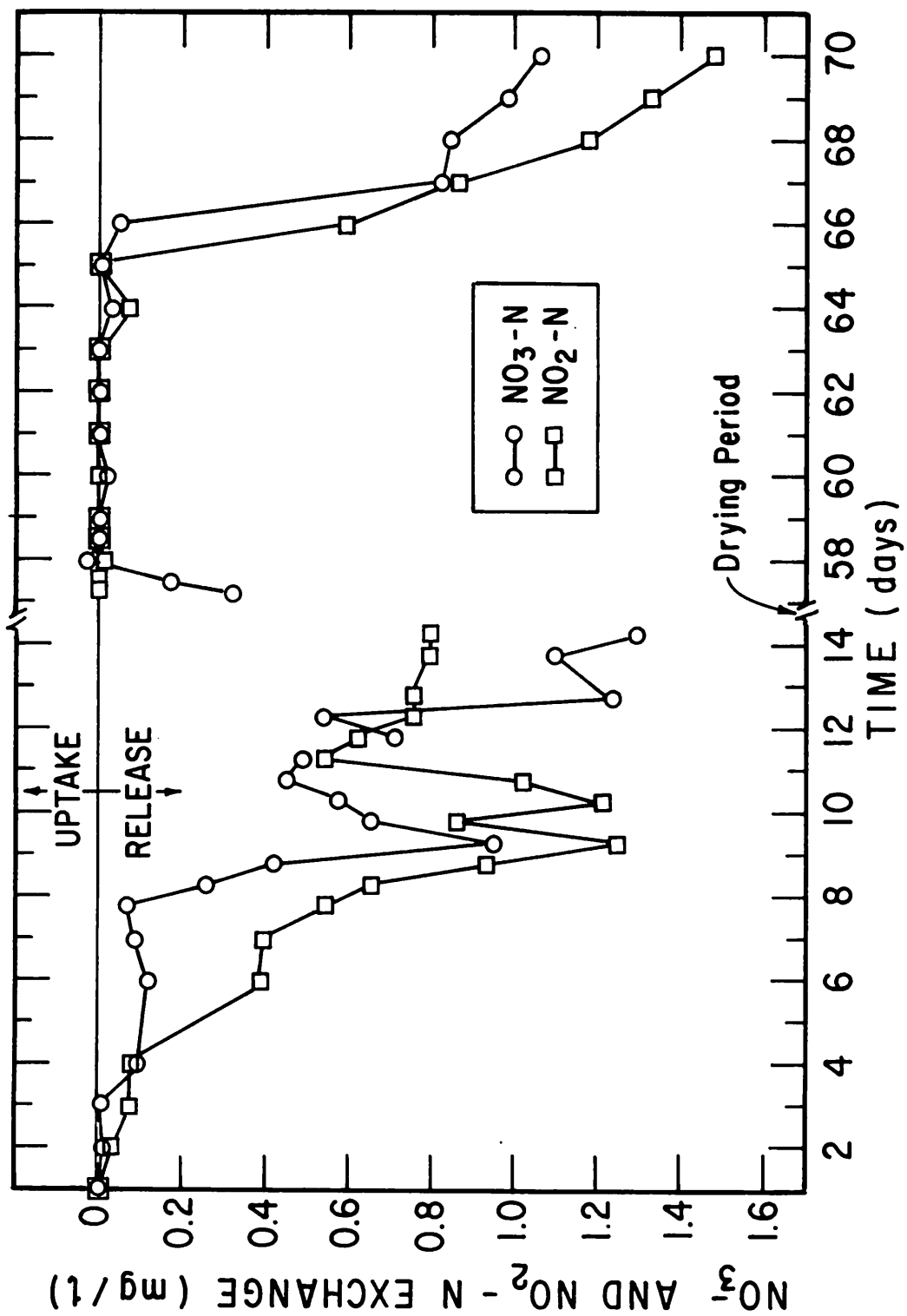
FIG. 7. NITROGEN EXCHANGE IN MICROCOSM 2 (MARSH GRASS-SEDIMENT - SPIKED)

uptake (Figure 6).

Phosphorus was taken up by the microcosm for the first two weeks (0.0 - 1.0 mg/l) (Figure 8). It was released for three to four days after the drying period after which uptake resumed.

Release of TOC during week two remained in the range of 2 - 4 mg/l (Figure 8). A high release was observed during the first twelve hours of reinundation after drying. After this time release returned to its initial range.

Marsh Grass Community : Microcosm 3

This microcosm consisted of the same components as the previous ones; however, the sediments were sealed from the overlying water by a layer of paraffin. (Nutrient concentrations were low.)

Ammonia nitrogen was taken up throughout the initial two-week period (Figure 9). By day 5, all ammonia in the influent was being taken up by the system. There was a release of ammonia for eighteen hours following the drying period after which ammonia was again taken up as it was prior to drying. Organic nitrogen was released during the entire study with an increase in the amount released for the initial twenty-four hours following the period of drying (Figure 9). There was a release of nitrite immediately after the drying period (Figure 9). Aside from this, no nitrite or nitrate were detected in the microcosm. The net exchange of nitrogen with the water was one of release except during the first forty-eight hours of reinundation after the "drought" (Figure 9).

FIG. 8. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 2
(MARSH GRASS–SEDIMENT – SPIKED)
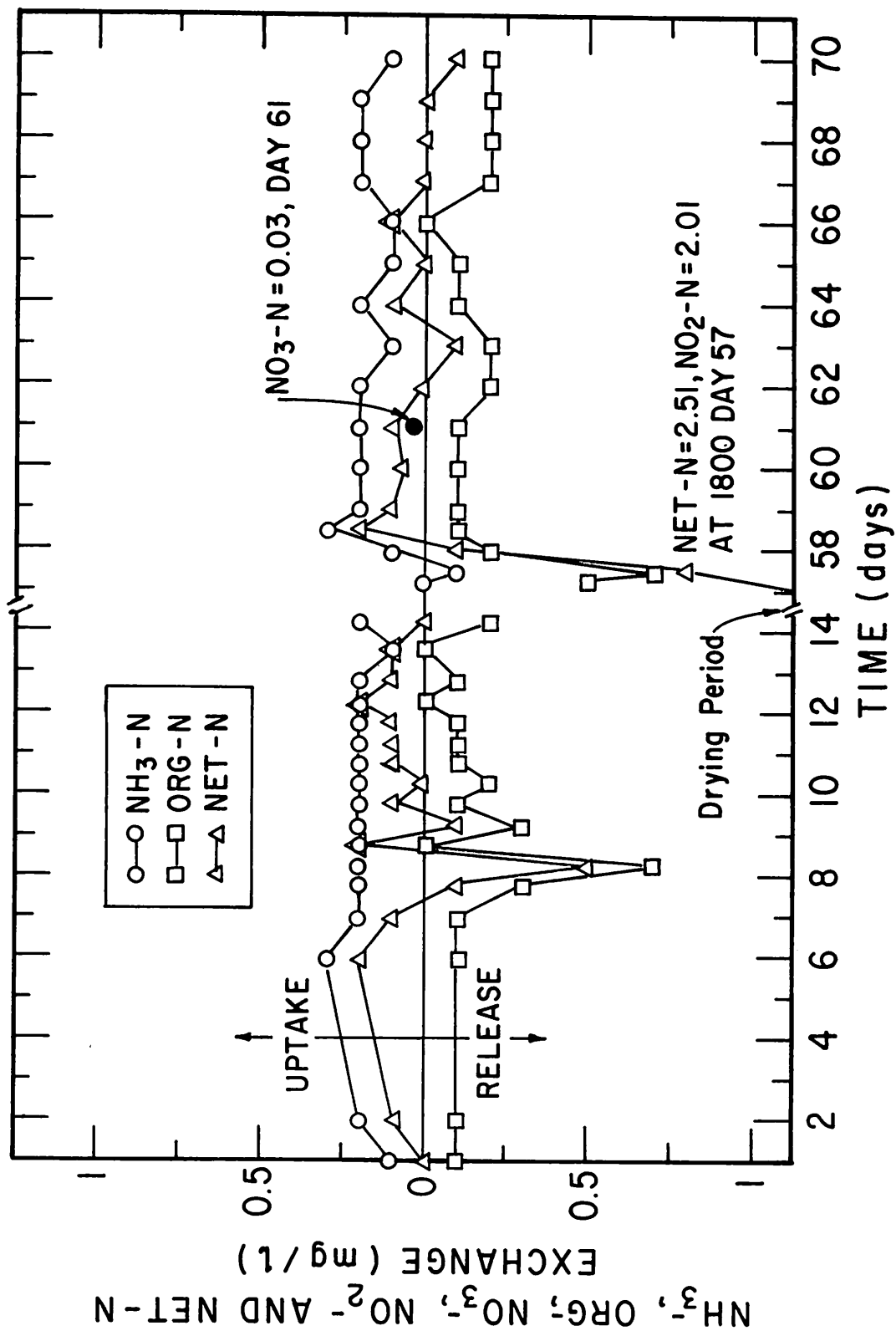
FIG. 9. NITROGEN EXCHANGE IN MICROCOSM 3 (MARSH GRASS – PARAFFIN – UNSPIKED)

Slight amounts of phosphorus were intermittently released and taken up in the initial two-week period (Figure 10). There was an initial release of phosphorus after the drying period for twelve hours, after which low amounts of phosphorus (0.0 - 0.04 mg/l) were taken up.

Carbon release was in the range of 0.1 - 6.8 mg/l during the second week (Figure 10). Following the drying period there was a large release for twelve hours followed by continuing release of from 0.1 - 3.9 mg/l during the remainder of the study.

Marsh Grass Community : Microcosm 4

This microcosm was the same as the previous one with the exception that additional nutrients were in the inflow water (additional 5 mg/l NH_3; 2 mg/l PO_4).

Initially, ammonia nitrogen was released from this system for a four-day period (in the first two weeks of the study) (Figure 11). Beginning on day 5 from 0.8 - 2.2 mg/l of ammonia were taken up for the remainder of the two weeks prior to drying. Immediately following the drying period, ammonia was released for twelve hours and then taken up. The amount of ammonia taken up decreased during the last week and on the last day ammonia was released. Organic nitrogen was taken up in the beginning of the study (Figure 11). For the remainder of the study, including the two-week recovery period after drying, it was intermittently released. Slight increases of nitrate were observed within the first three days following the drying period (Figure 11). Nitrate was not detected in this microcosm
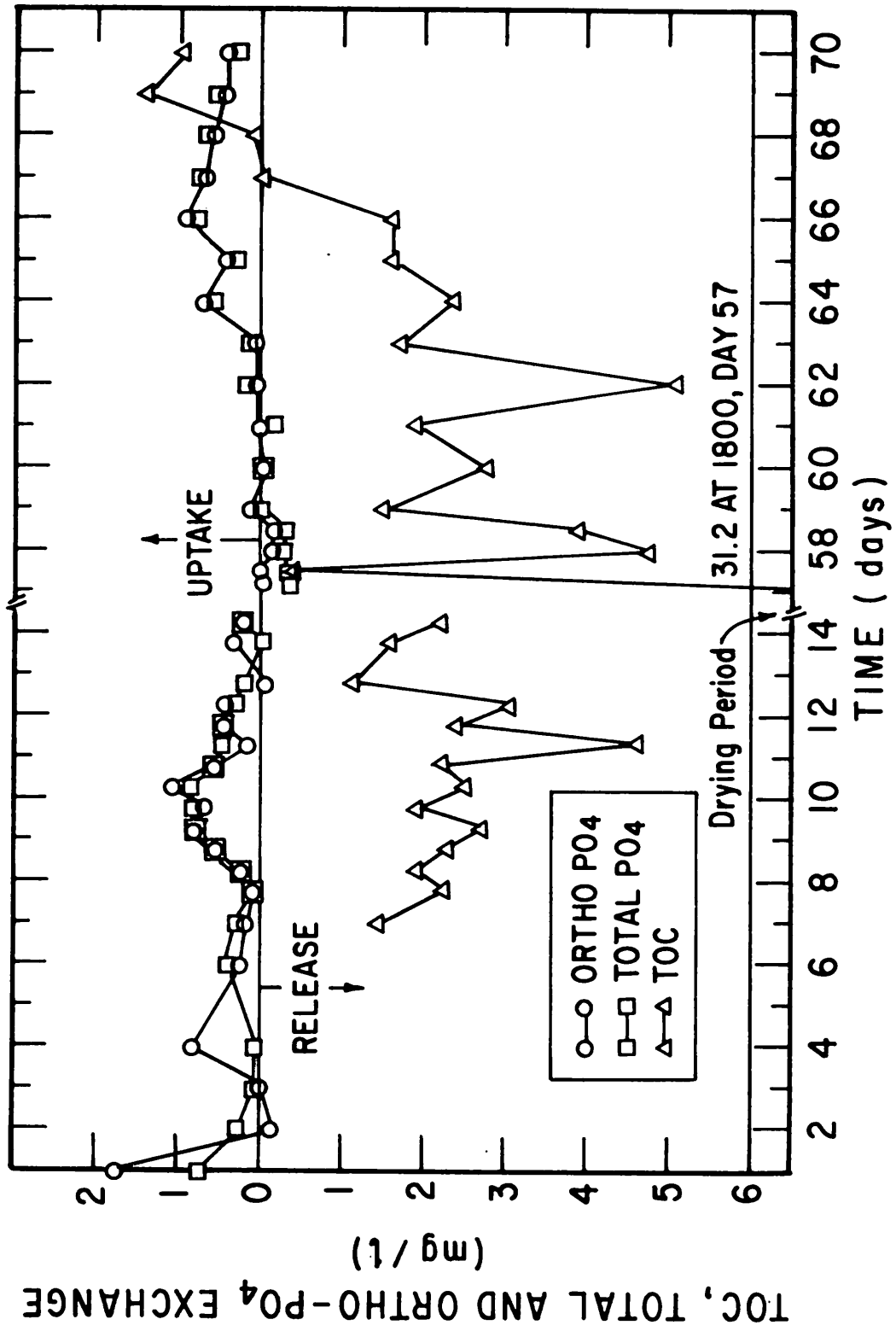
FIG. 10. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 3
(MARSH GRASS-PARAFFIN – UNSPIKED)
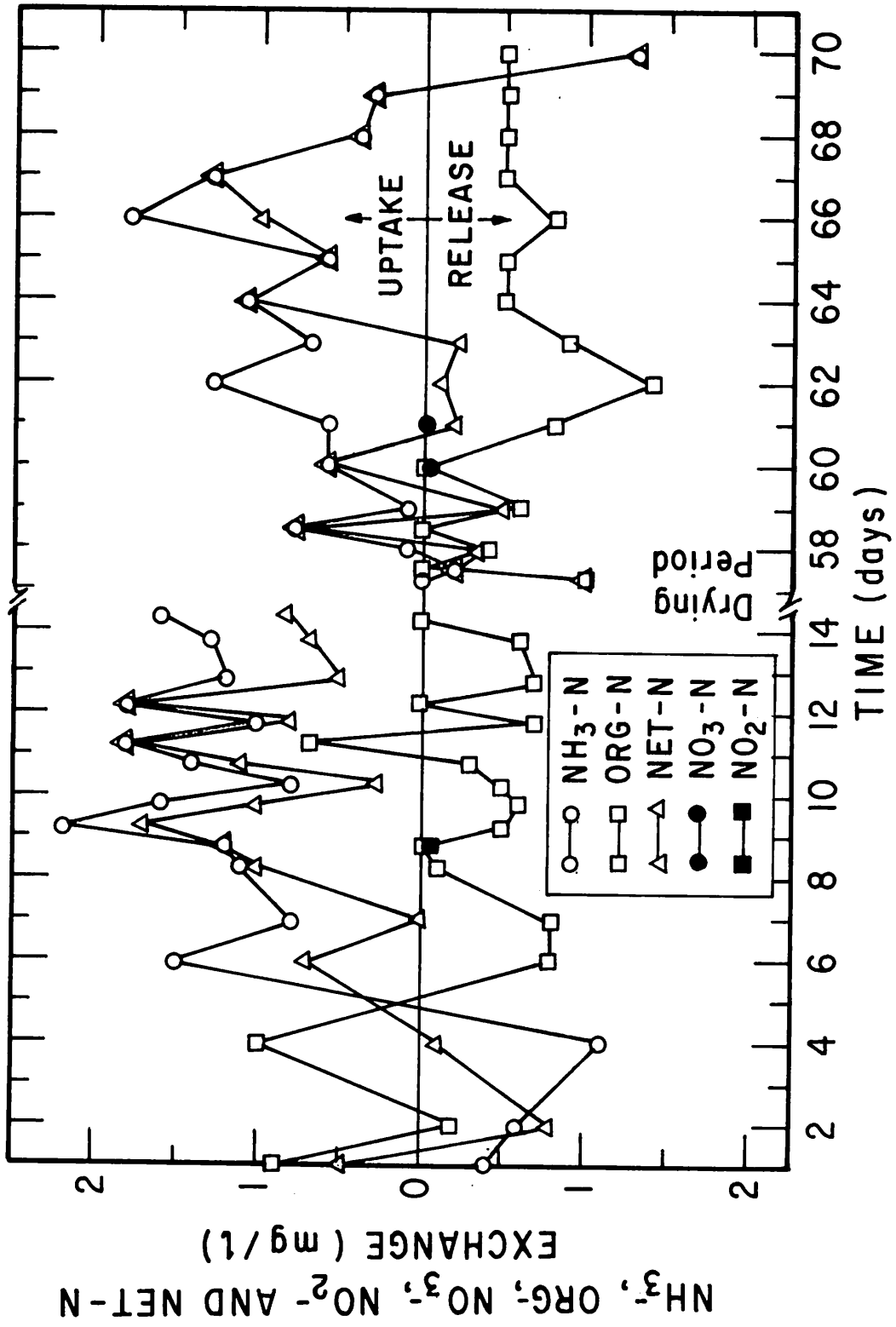
FIG. 11. NITROGEN EXCHANGE IN MICROCOSM 4 (MARSH GRASS-PARAFFIN – SPIKED)

at any other time, and nitrite was not detected at all during the study.

Phosphorus was taken up the first week, released for twenty-four hours when the water level was lowered at the beginning of week two and then taken up again (Figure 12). After the drying period, release and uptake were intermittent for the first five days. Following this time, phosphorus was again taken up but at a lower rate than was observed before the drying period.

From 0.3 - 4.2 mg/l of TOC were released in the second week of the study (Figure 12). Immediately following the drying period, release was higher for twelve hours and then returned to the range observed in week two.

ALGAL MAT MICROCOSMS

Algal Mat Community : Microcosm 5

This microcosm contained the algal mat (Lyngbya confervoides primarily) and underlying sediment as well as the microorganisms that were present in either the sediment, algae, or water when the sample was removed from the marsh.

On the sixth day of the study, a slight amount of ammonia was released (Figure 13). No other ammonia exchange was observed during the first week. During the second week, ammonia was released. After the drying period it was released in amounts exceeding those previous to drying. Organic nitrogen was released for the first two weeks with the release being higher during the second week (Figure 13).
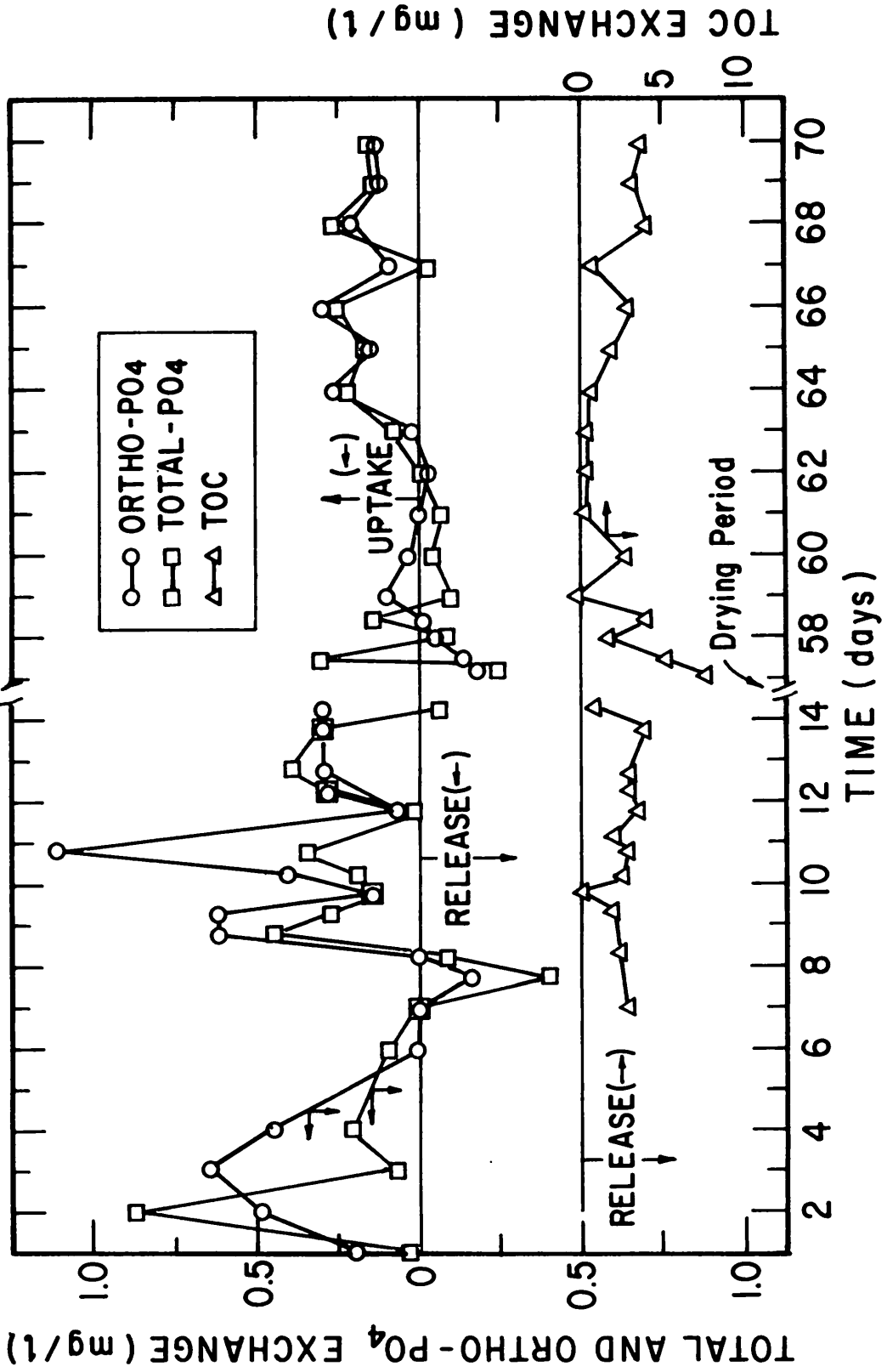
FIG. 12. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 4
(MARSH GRASS-PARAFFIN – SPIKED)

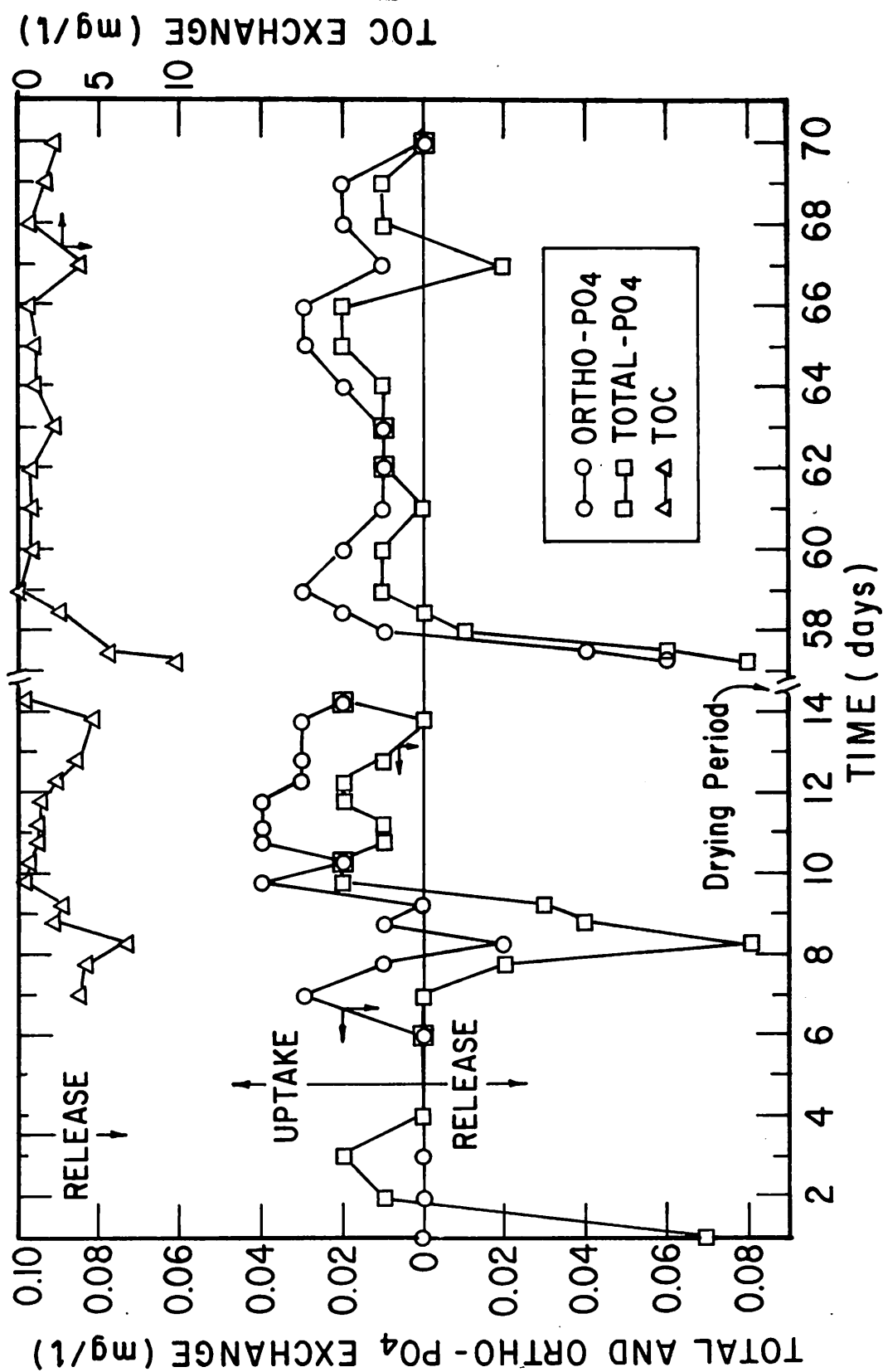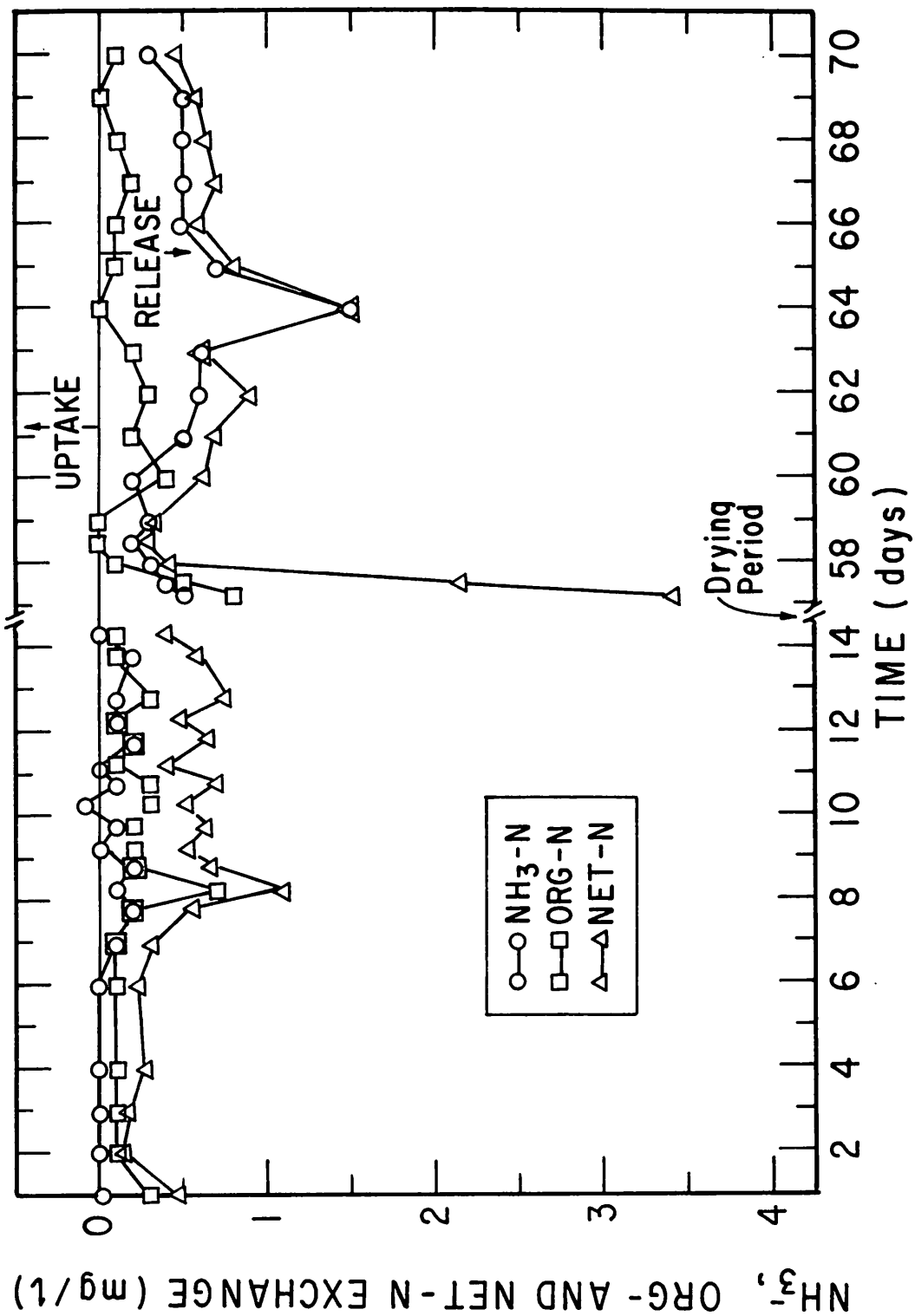FIG. 13. NITROGEN EXCHANGE IN MICROCOSM 5 (ALGAL MAT - UNSPIKED)

Following the period of drying 0.4 - 0.8 mg/l of organic nitrogen were released for the initial twelve-hours after which less was released for the remainder of the recovery period. Nitrite was released in small amounts (0.0 - 0.04 mg/l) in the first two-week period (Figure 14). Nitrate was also released during this time with the amount of release increasing in the second week (Figure 14). After the drying period, small amounts of nitrite were released for eighteen hours after which no further release was noted. Nitrate was initially released at a higher rate than during the wet period for twelve hours, at a lower rate for two days, and no exchange occurred again until day 68 when release was resumed. The net exchange of nitrogen was one of release throughout the study (Figure 13).

From 0.0 - 0.2 mg/l of phosphorus were released during the first two-week period (Figure 15). Phosphorus was released again for ten days following the drought period, no exchange occurred for two days and a slight amount was taken up on the last day.

Carbon was released during the second week of the study (1.0 - 3.5 mg/l) (Figure 15). Following the drying period, 4.5 - 9.5 mg/l were released for twelve hours and 0.6 - 4.5 mg/l of TOC were released throughout the remainder of the post-drying period.

Algal Mat Community : Microcosm 6

This microcosm contained the same components as the previous one, the only difference being that the influent water in this case contained additional amounts of nitrogen and phosphorus (additional 5 mg/l NH_3; 2 mg/l PO_4).

FIG. 14. NITROGEN EXCHANGE IN MICROCOSM 5 (ALGAL MAT – UNSPIKED)
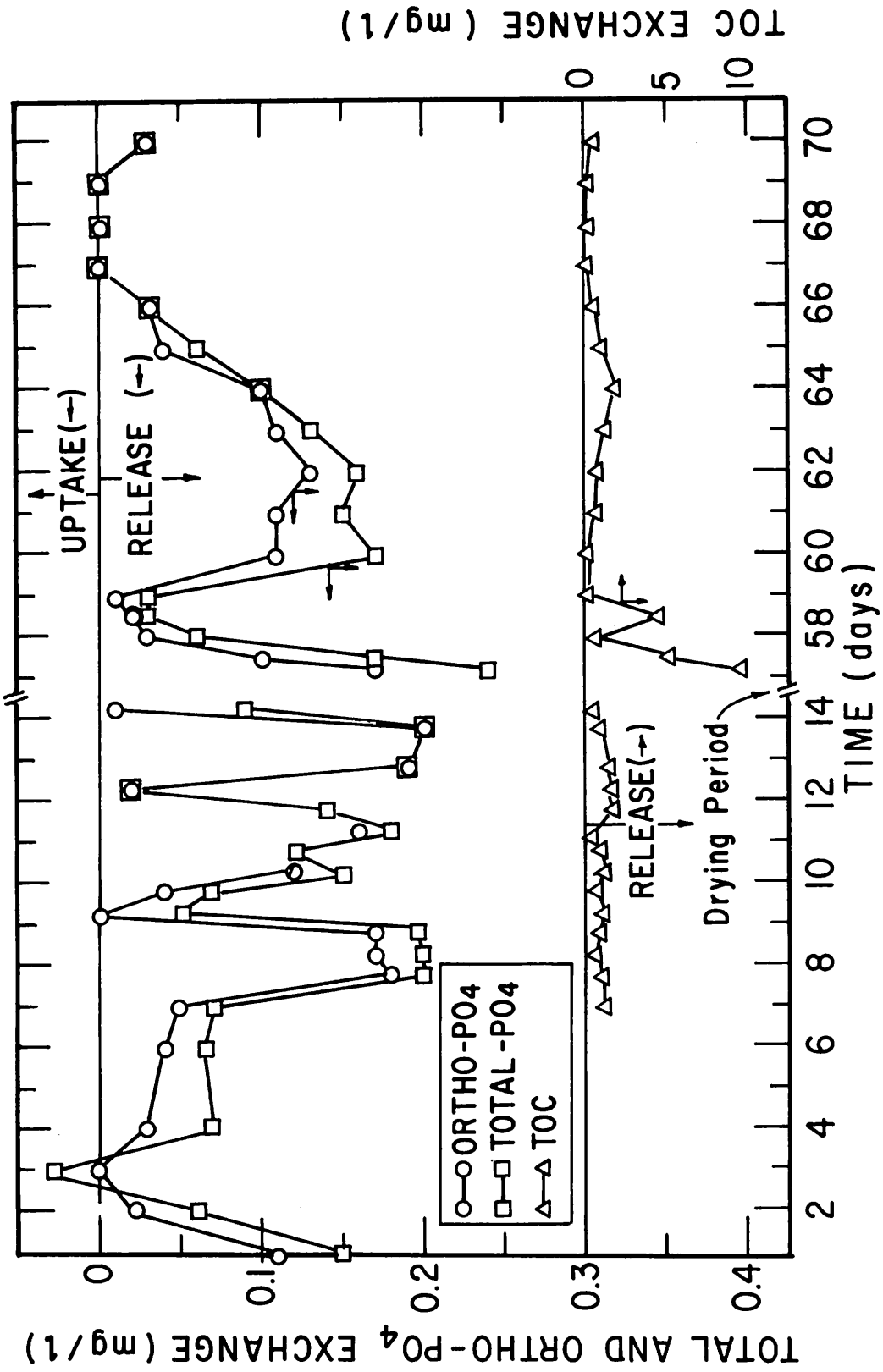
FIG. 15. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 5
(ALGAL MAT – UNSPIKED)

Ammonia was taken up during the first two weeks (Figure 16).
The amount taken up increased during the second week (except for
a low release when the water level was changed). Following the
drying period, ammonia was intermittently released and taken up for
seven days after which uptake occurred and continued to increase
reaching 3.0 mg/l by the end of the recovery period. Organic nitrogen
was intermittently released and taken up during the first two-week
period (Figure 16). In the two weeks following the drying period,
its exchange alternated between release and no exchange. Both
nitrate and nitrite were released in the first two weeks (Figure 17).
A large amount of nitrate was released for twelve hours following the
drying period and a decreasing amount was released for the next
twenty-four hours. After this initial release, no nitrate release
occurred until the beginning of the second week. From that time on
nitrate release increased to the end of the study. Nitrite was re-
leased from twelve to twenty-four hours after the end of the drying
period. There was no subsequent nitrite release until the end of the
first week after drying from which time on the amount of nitrite released
increased. The net exchange of nitrogen was primarily one of uptake
for the first two weeks, release for the nine days immediately fol-
lowing the drying period, and returned to uptake at the end (Figure
16).

Phosphorus was taken up for the first three days of the study
and not exchanged for the remainder of the first week (Figure 18).
Total phosphate and orthophosphate were both taken up and released
during the second week. After the drying period, phosphorus was
alternately released and taken up for a four-day period. After this
initial four-day period, it was taken up increasingly to the end of
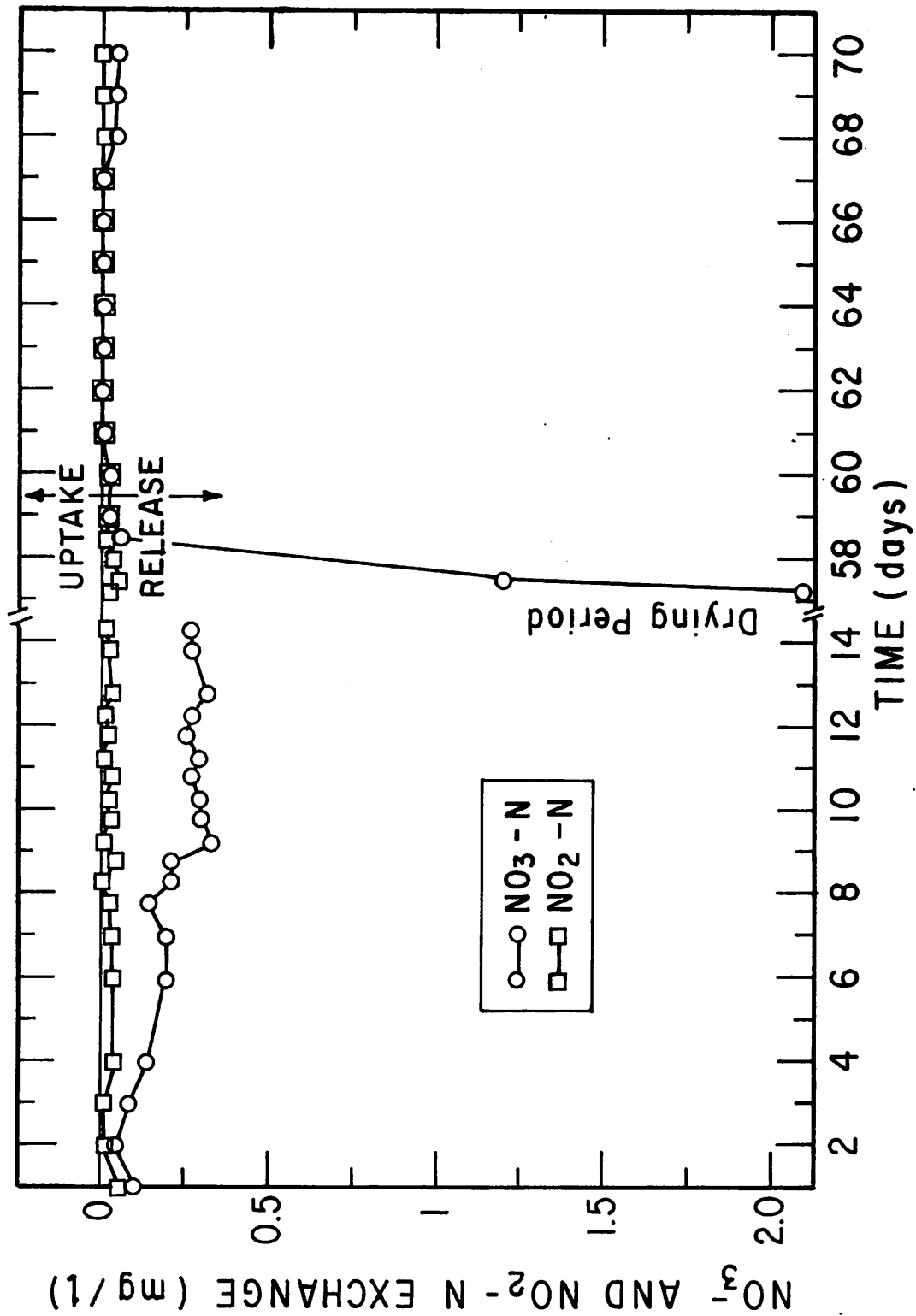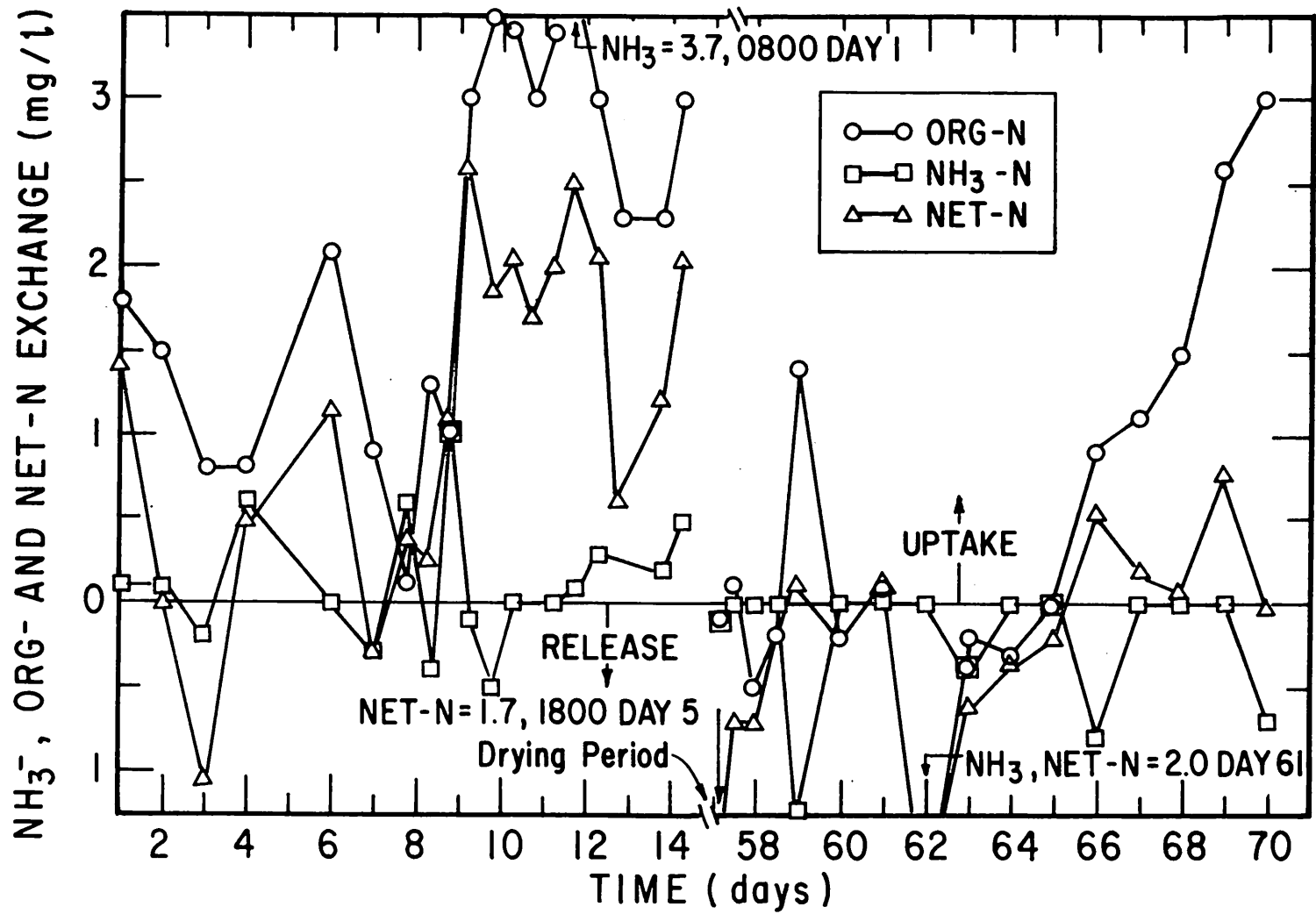
FIG. 16. NITROGEN EXCHANGE IN MICROCOSM 6 (ALGAL MAT - SPIKED)
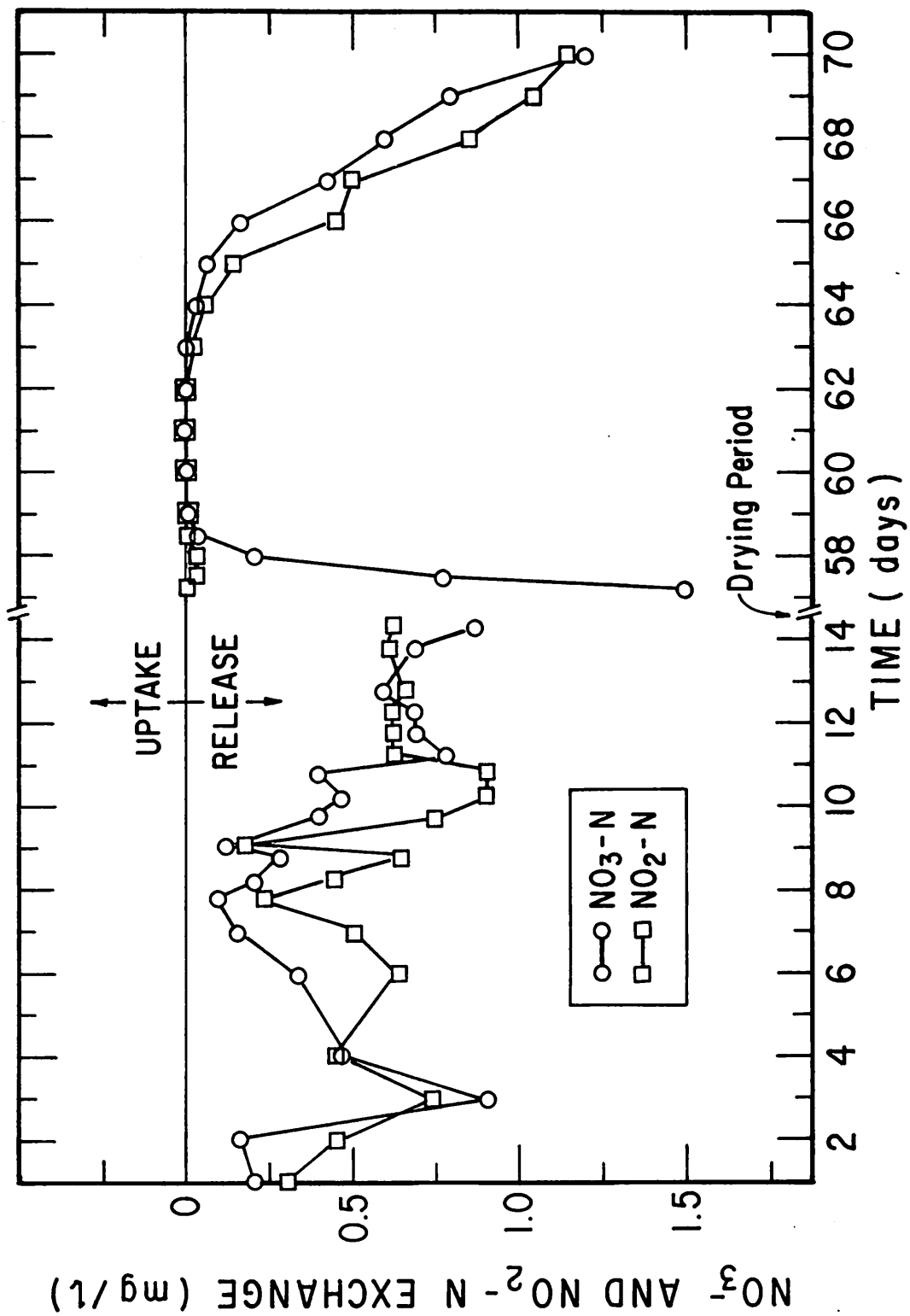
FIG. 17. NITROGEN EXCHANGE IN MICROCOSM 6 (ALGAL MAT – SPIKED)
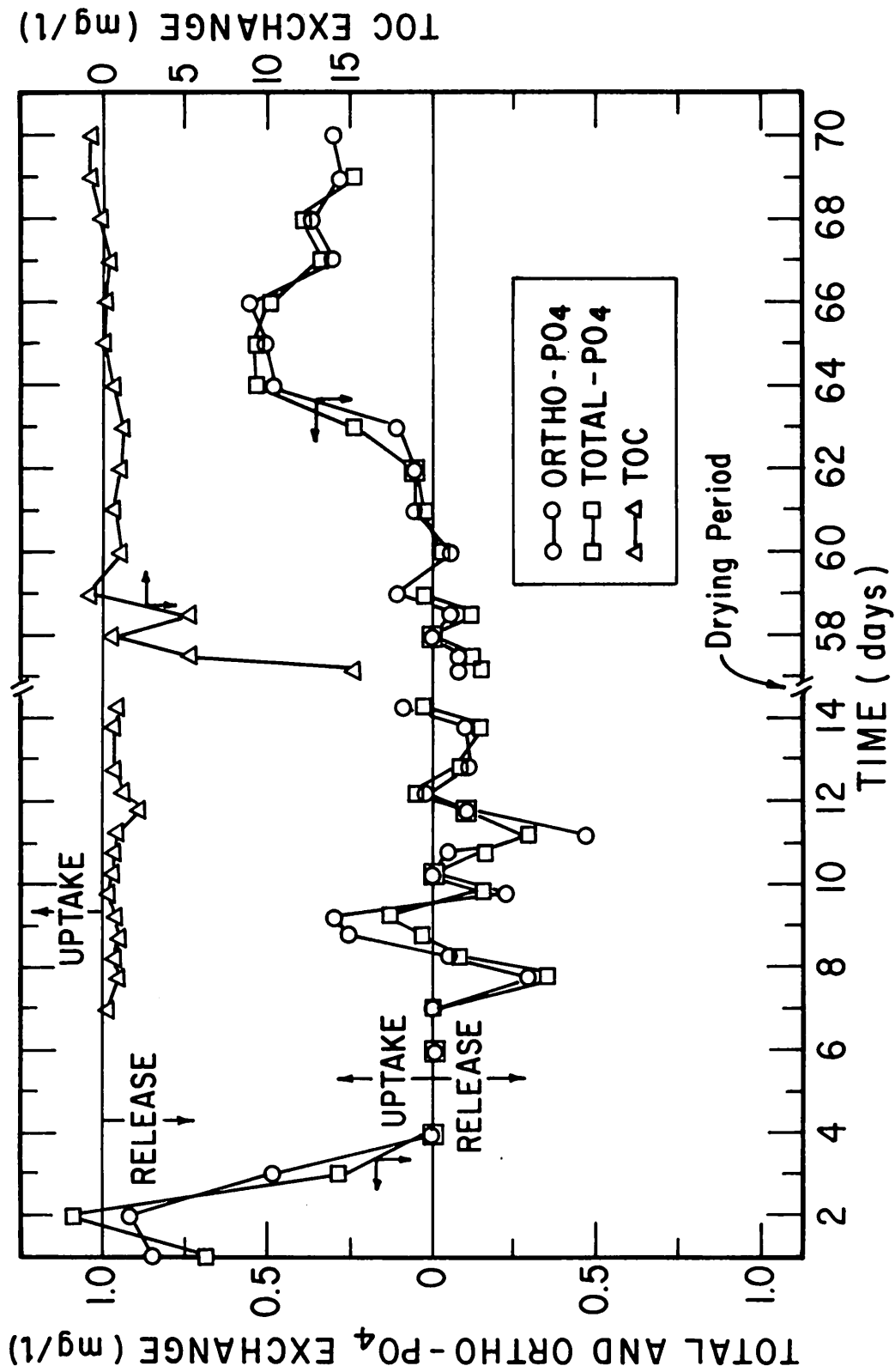
FIG. 18. CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 6 (ALGAL MAT – SPIKED)

that week and then uptake decreased slightly but continued.

Release of carbon ranged from 0.2 - 2.25 mg/l of TOC during the second week of the study prior to drying (Figure 18). After the drying period there was an initially higher release for twenty-four hours after which release remained from 0.0 - 5.7 mg/l. (At two points following the drying period, organic carbon was taken up. This may be due to organic growth in the influent water or to laboratory error.)

RATE AND CUMULATIVE MASS OF NUTRIENTS EXCHANGED

Marsh Grass - Sediment Community : Microcosm 1 (Unspiked)

Ammonia nitrogen and organic nitrogen were exchanged at fairly constant rates during week one (four-inch water level) and appeared to be at steady state conditions (Figure 19). Both these rates were lower during week two (water level was lowered to one inch at the beginning of week two). After the drying period, ammonia and organic nitrogen exchange appeared to reach steady state by day 63. Nitrate and nitrite nitrogen were exchanged at constant rates (steady state) throughout the study except during the first week after the drying period when no exchange occurred. The net nitrogen exchange reached steady state by day 4 during the initial two week period and by day 62 after the drying period.

Orthophosphate and total phosphate were exchanged at constant rates (steady state) during the first two weeks, with the rate of exchange being lower the second week (Figure 20). After the drying

FIG. 19. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 1
(MARSH GRASS-SEDIMENT – UNSPIKED)
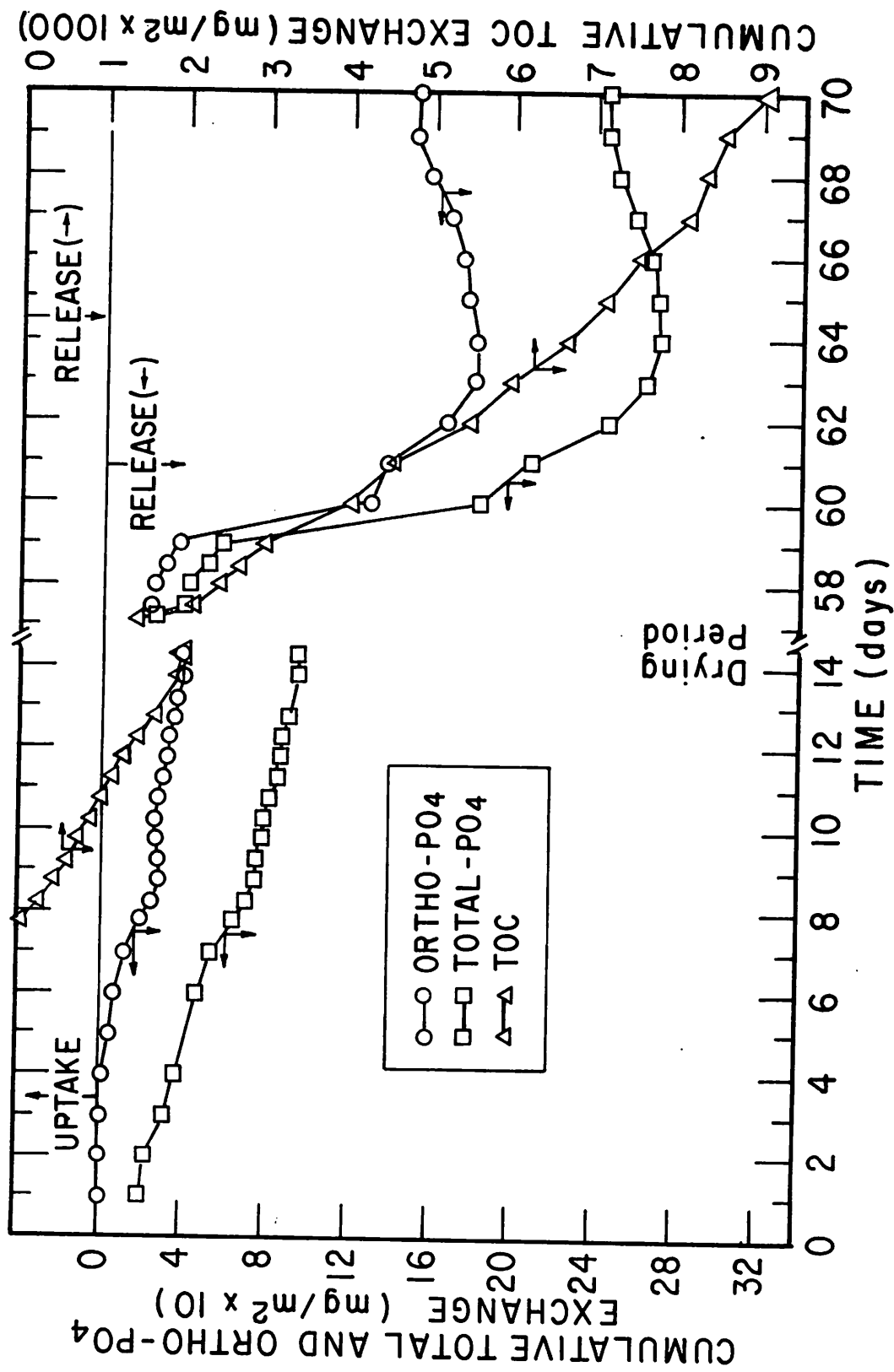
FIG. 20. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 1
(MARSH GRASS–SEDIMENT – UNSPIKED)

period both were released for a week after which uptake occurred and both appeared to reach equilibrium at the end of the second week after drying.

Total organic carbon was released at a constant rate (steady state) throughout the study except during the initial twenty-four hours after drying when release was much higher than at any other time (Figure 20). The rate of release was lower during the second week than it was after the drying period.

Marsh Grass - Sediment Community : Microcosm 2 (Spiked)

Ammonia nitrogen was taken up at a relatively constant rate (steady state) during the first two weeks (Figure 21). This rate was slightly lower during the second week than the first (water level was lower during week two). After the drying period ammonia was released for a week after which uptake occurred at a constant rate (steady state) for the remainder of the study. Organic nitrogen exchange was inter-mittent the first week but appeared to be at equilibrium the second. After drying, organic nitrogen was released at a high rate for three days and was released at a constant rate (steady state) for the re-mainder of the study. Nitrate and nitrite were released at a constant rate (steady state) during weeks one and two (lower rate during week two). After drying, there was an initial release of nitrate and nitrite, no release for several days, and on day 65 release was resumed and continued at a constant rate (steady state) to the end of the study. This final nitrate and nitrite release coincided with the final uptake of ammonia. The net nitrogen exchange paralleled that of ammonia throughout the study.
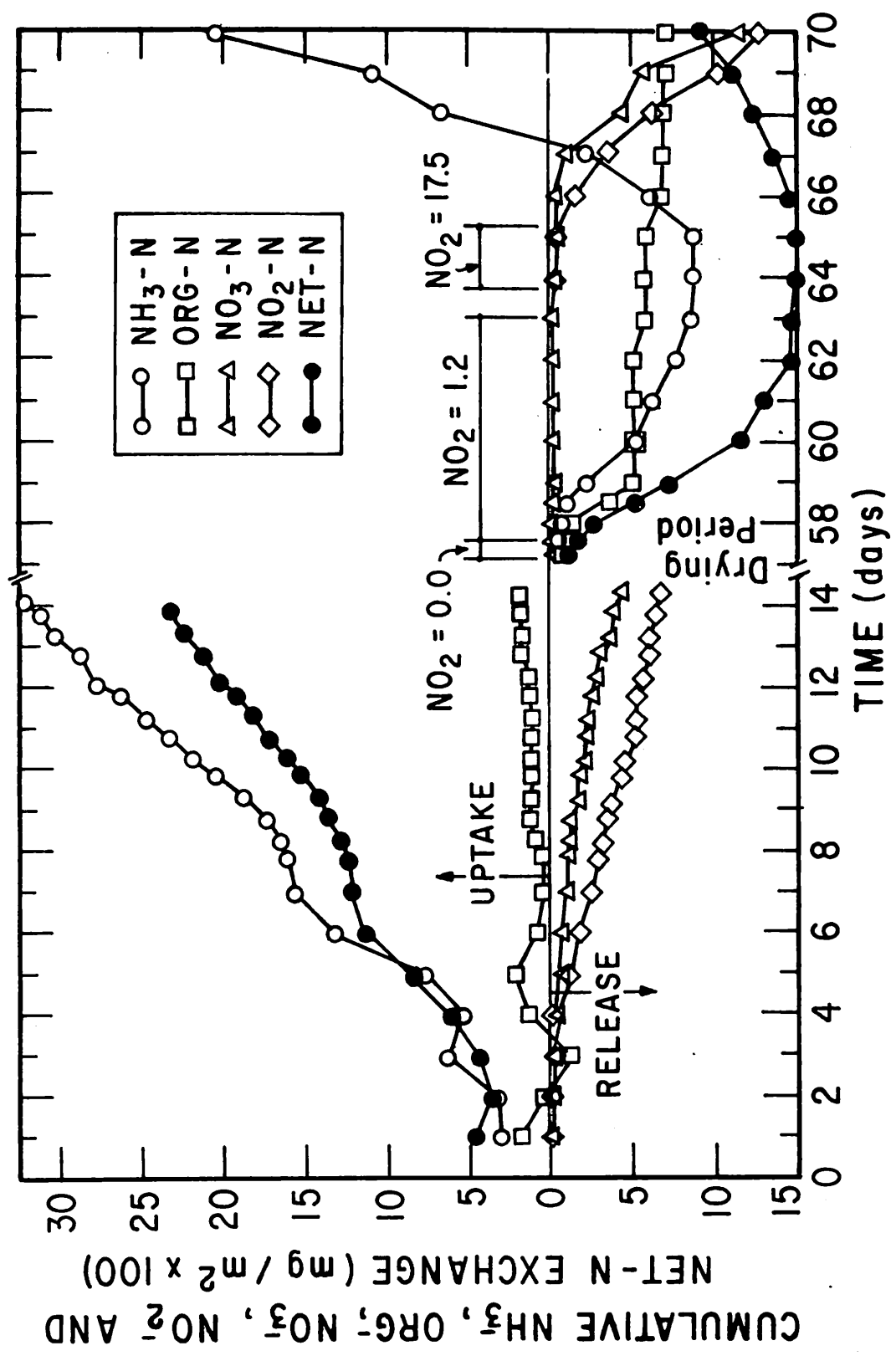
FIG. 21. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 2
(MARSH GRASS-SEDIMENT - SPIKED)

Orthophosphate was taken up at a relatively high, constant rate from day 4 to day 7 (Figure 22). Uptake continued during week two, but was at a lower rate during the second week than the first. Both orthophosphate and total phosphate were initially released for several days after the drying period. Uptake of both occurred from day 62 to the end of the study at a constant rate (steady state) comparable to that of week one.

Total organic carbon was released at a lower rate during week two than it was after the drying period (Figure 22). By day 66 its exchange appeared to be approaching equilibrium.

Marsh Grass Community : Microcosm 3 (Unspiked)

Ammonia nitrogen was taken up at a constant rate (steady state) by day 3 (Figure 23). The rate of uptake was lower the second week but remained constant. The rate of release of ammonia was constant after the drying period and approximately the same as it had been at the end of week one. Organic nitrogen was released at a constant rate (steady state) by day 3 of the first week and continued at that rate for the remainder of the week. The release rate was lower the second week but remained constant. After the drying period, the re-lease of organic nitrogen occurred at a constant rate by day 58. The net nitrogen exchange appeared to be at equilibrium by day 6 of the study before drying and by day 60 after the drying period.

Orthophosphate was not exchanged for the first six days of the study (Figure 24). It was taken up during the second week and this uptake occurred at a constant rate (steady state) by day 9. After

FIG. 22. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 2
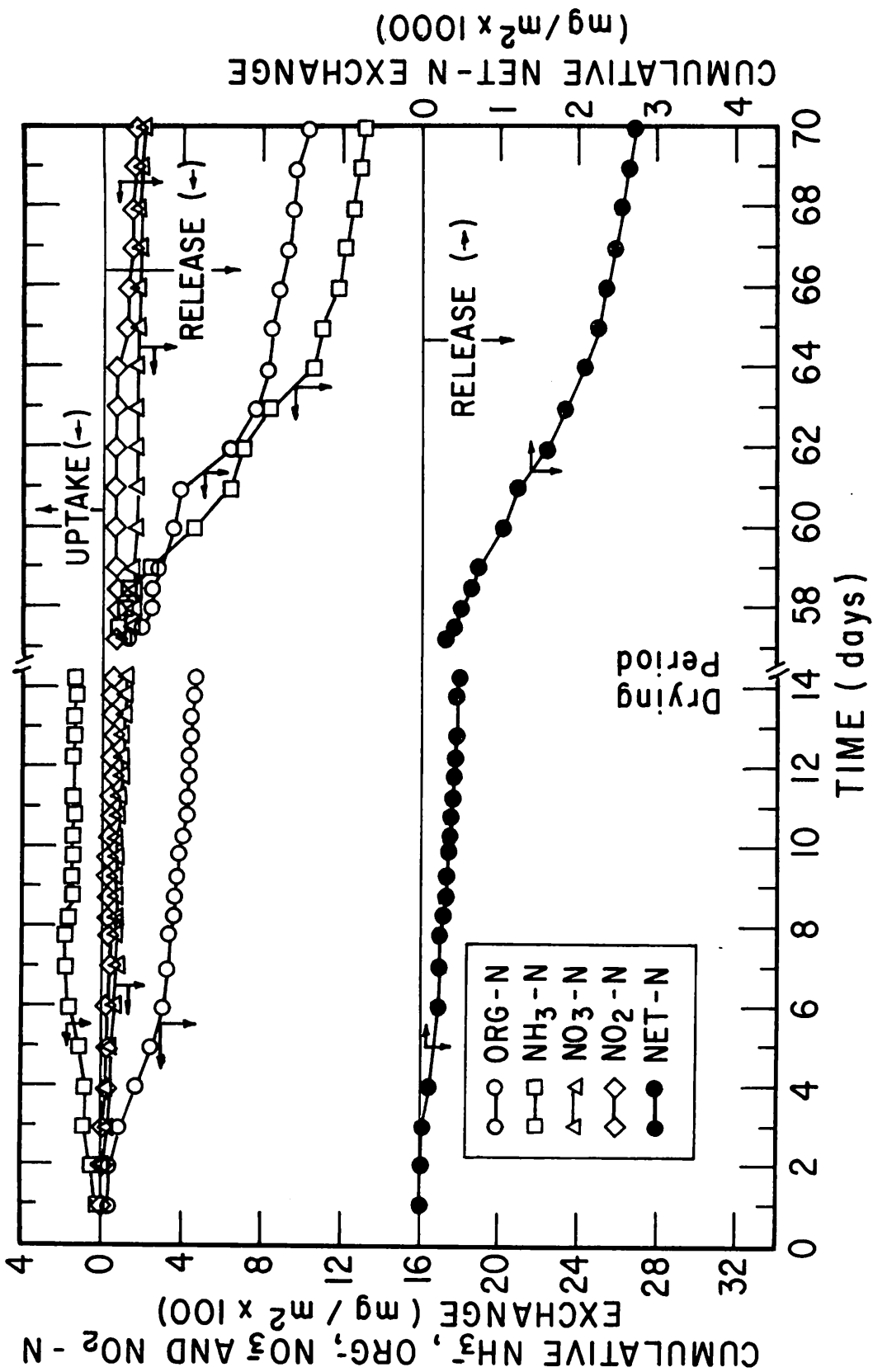(MARSH GRASS-SEDIMENT - SPIKED)

FIG. 23. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 3
(MARSH GRASS–PARAFFIN – UNSPIKED)
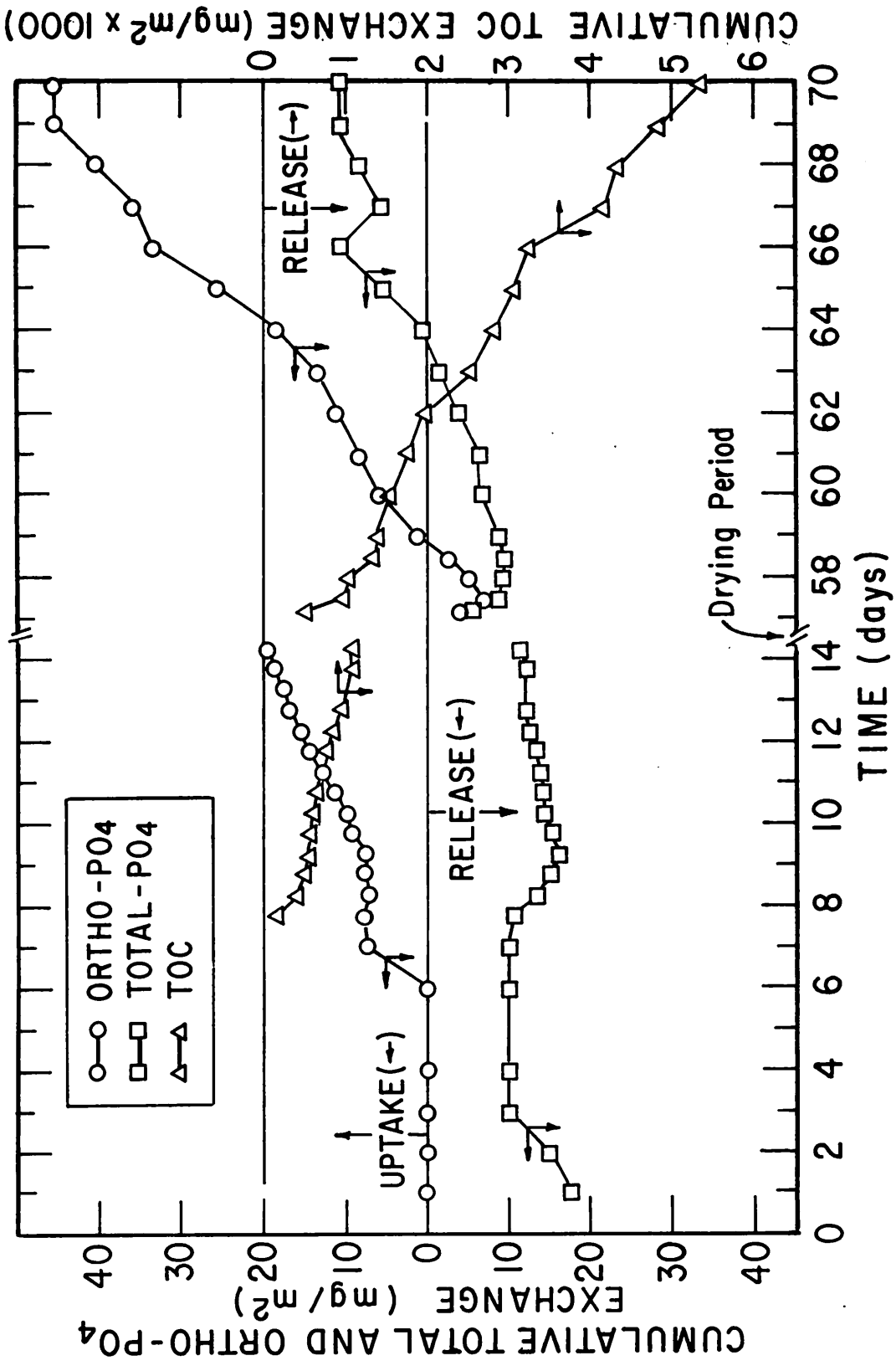
FIG. 24. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 3
(MARSH GRASS-PARAFFIN – UNSPIKED)

drying, a higher constant rate of uptake occurred following the initial twenty-four hour period. Total phosphate exchange was one of release during the first two weeks, a constant release rate being reached by day 9. After drying, total phosphate was released for twenty-four hours and taken up at a constant rate (steady state) beginning on day 59. The total phosphate exchange reached equilibrium during the last four days of the study.

Total organic carbon was released at a constant rate (steady state) throughout the study except for the initial twelve-hour period after drying (Figure 24). This occurred at a lower rate during week two than it did after drying.

Marsh Grass Community : Microcosm 4 (Spiked)

Ammonia nitrogen was released in the beginning of week one and taken up at a constant rate (steady state) the last three days of the week (Figure 25). Uptake continued at a constant rate during week two, but this was a lower exchange rate than that of week one. Ammonia was taken up at a constant rate (steady state) after the drying period and appeared to approach equilibrium at the end of the study. Organic nitrogen was intermittently taken up and released during week one and was released at a constant rate (steady state) during week two. After drying, it was again released. Net nitrogen exchange occurred at a constant rate (steady state) the second week and by day 63 after the drying period. It appeared to approach equilibrium at the end of the study.
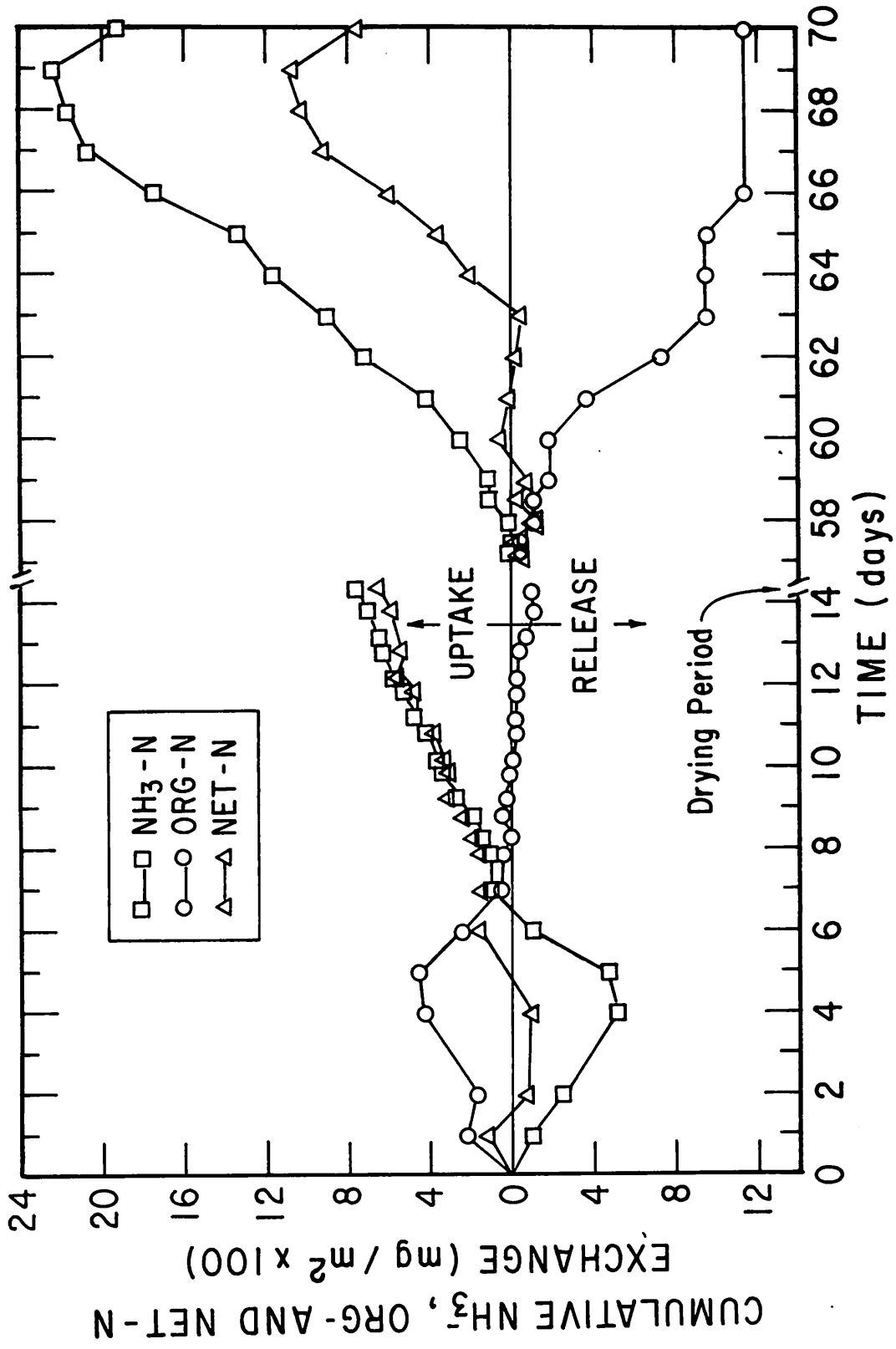
FIG. 25. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 4
(MARSH GRASS-PARAFFIN – SPIKED)

Orthophosphate and total phosphate were initially taken up at a relatively high constant rate (steady state) (Figure 26). Both were taken up at a lower constant rate the second week. After drying, a constant rate of uptake was attained by day 62.

Total organic carbon was released at a constant rate (steady state) during week two and after the drying period except during the initial twelve hours immediately following the drying period (Figure 26). The release rate during week two was lower than the release rate which occurred after drying.

Algal Mat Community : Microcosm 5 (Unspiked)

Little exchange of ammonia occurred during the first two weeks (Figure 27). After drying, it was released at a constant rate (steady state) from day 59 to the end of the study. Organic nitrogen and nitrate were released at a constant rate (steady state) the first week and the second week. The rate of release was lower during the second week. After drying, organic nitrogen was released at a constant rate by day 60. After drying, nitrate was initially released and no further release occurred until day 68. Little exchange of nitrite occurred during the study. Net nitrogen exchange was at a constant rate (steady state) during weeks one and two, but the rate of exchange was lower during week two. After drying, the net nitrogen exchange was at a constant rate by day 59.

Orthophosphate and total phosphate were released at constant rates (steady state) during the first two weeks (Figure 28). This rate was lower during the second week than the first. After drying, both
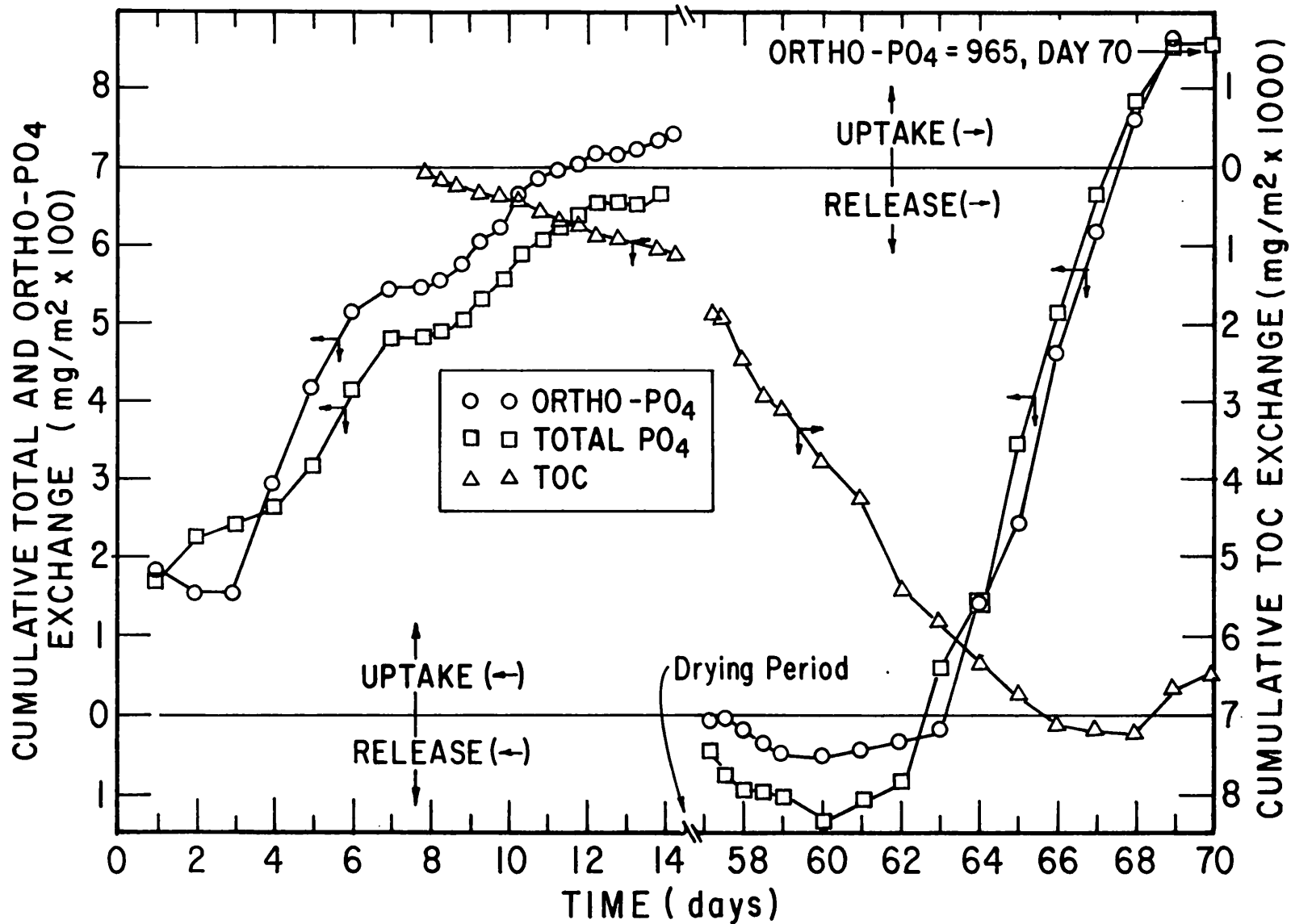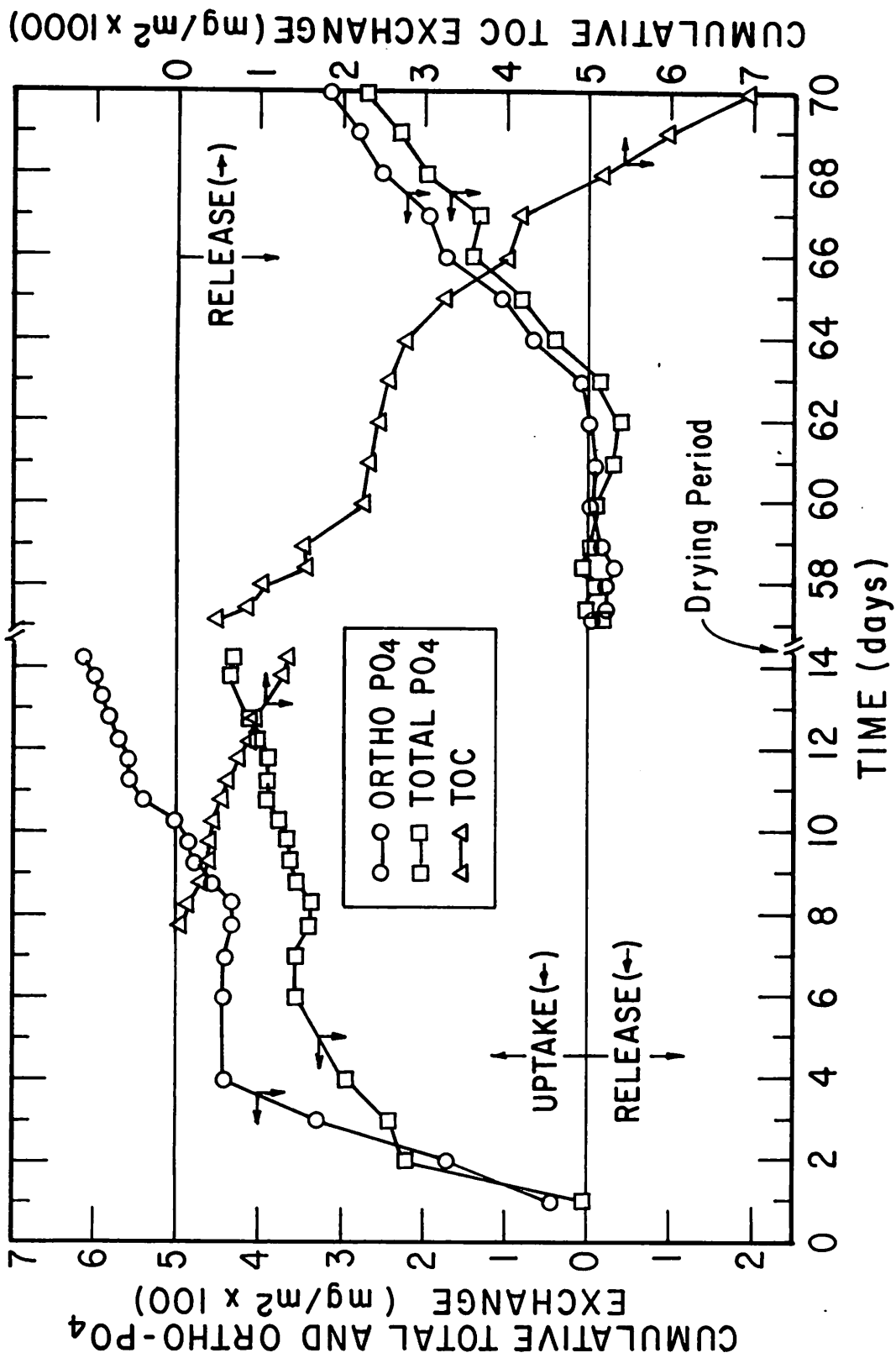
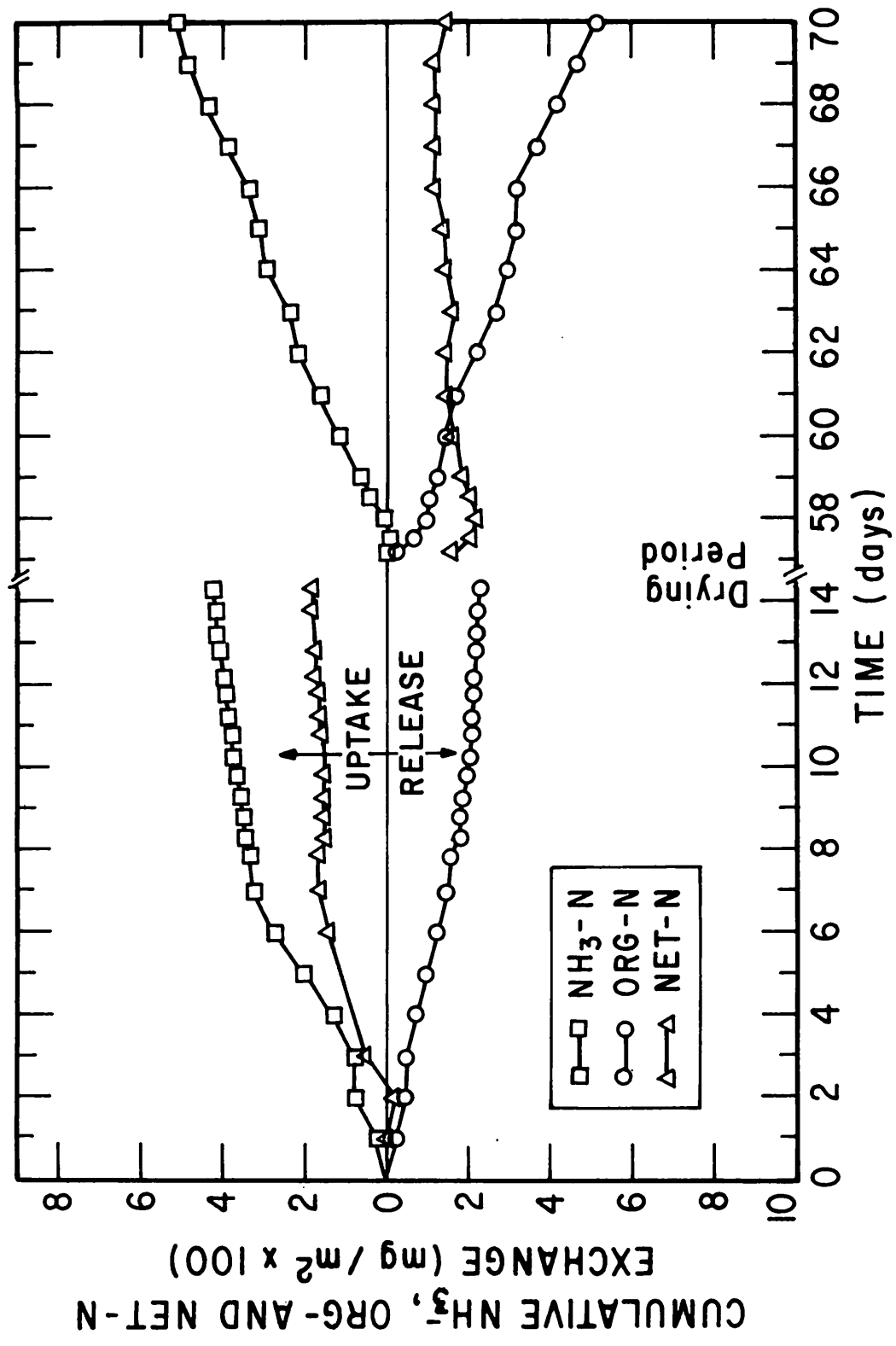FIG. 26. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 4
(MARSH GRASS-PARAFFIN – SPIKED)
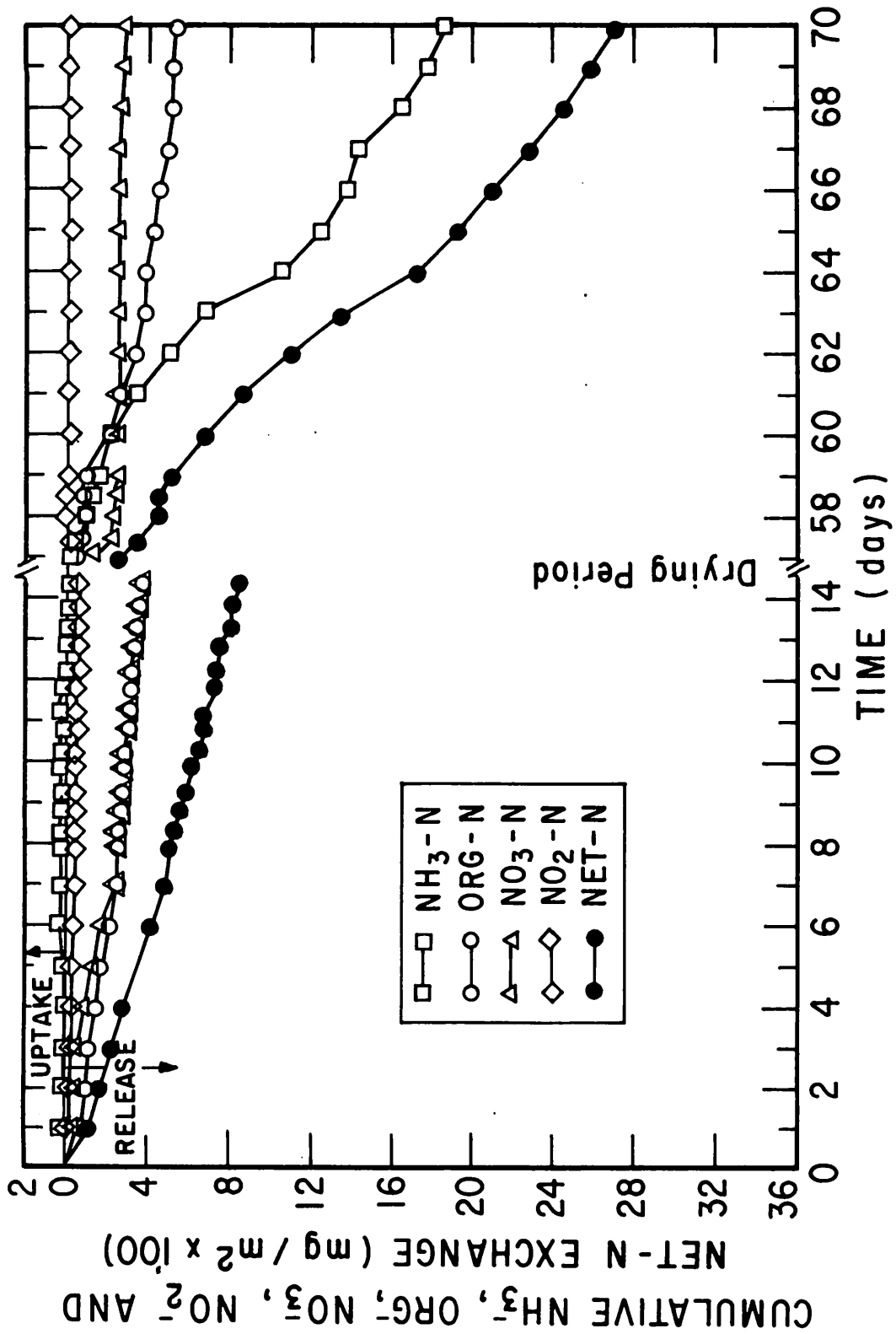
FIG. 27. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 5 (ALGAL MAT – UNSPIKED)
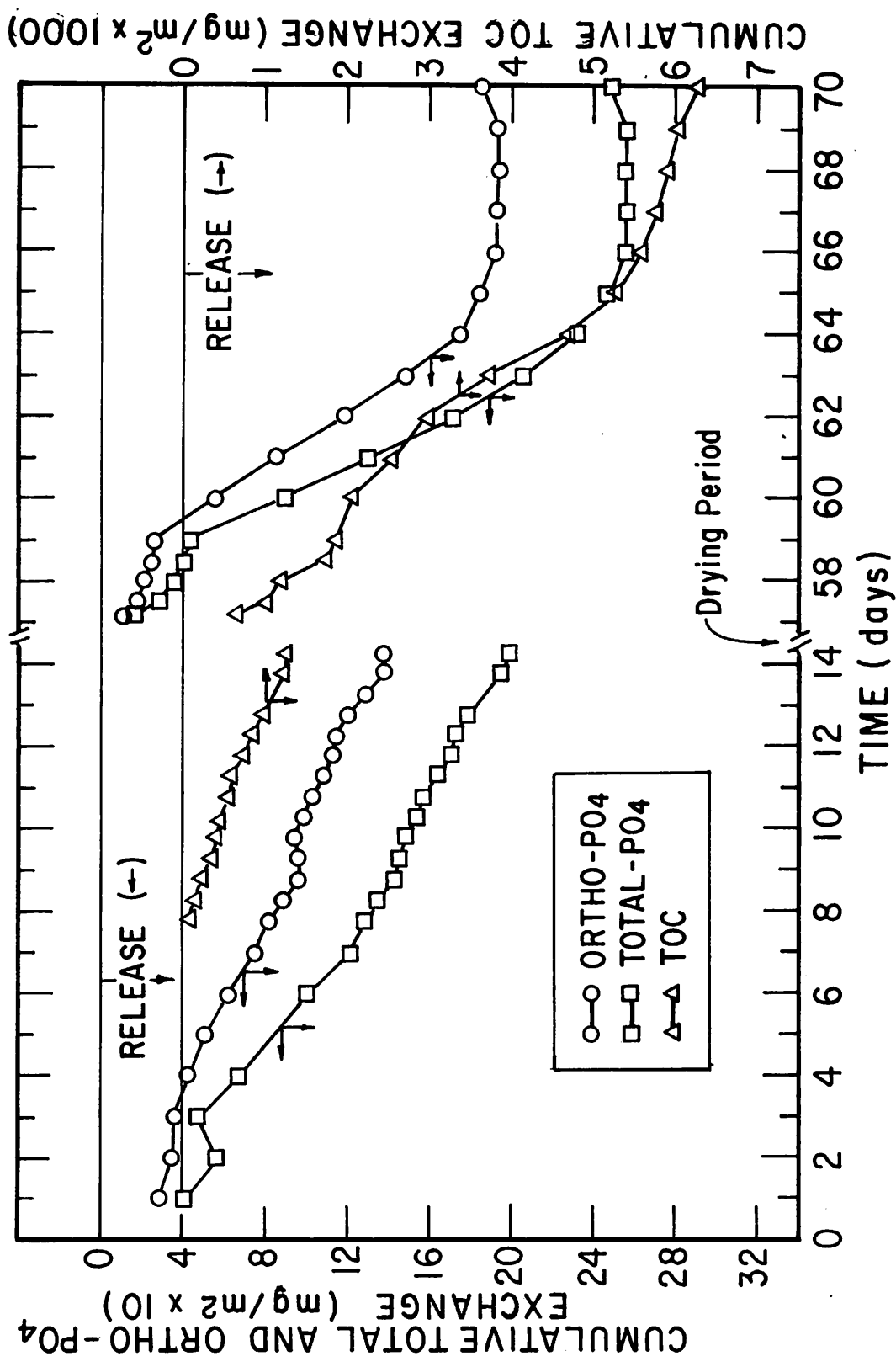
FIG. 28. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 5
(ALGAL MAT - UNSPIKED)

were released at a constant rate and appeared to approach equilibrium by day 64.

Total organic carbon was released at a constant rate (steady state) during week two (Figure 28). After drying, it was released at a constant rate by day 58.

Algal Mat Community : Microcosm 6 (Spiked)

Ammonia nitrogen was taken up at a constant rate (steady state) during weeks one and two (Figure 29). This rate was lower the second week than it was the first. After drying, ammonia was initially released and was taken up at a constant rate by day 65. Organic nitrogen was released and taken up during week one and was at equilibrium during week two. After drying, it was released at a relatively constant rate (steady state). Nitrate and nitrite were released at constant rates (steady state) during weeks one and two. This rate was lower the second week than it was the first. After drying, both nitrate and nitrite were initially released and no further exchange occurred until day 65. At this time a constant rate of release of both began (coinciding with resumed ammonia uptake) and continued for the remainder of the study. Net nitrogen exchange was constant during week two.

Orthophosphate and total phosphate were taken up during the first two days of the study, not exchanged for the remainder of week one and were exchanged at a constant rate (steady state) during week two (Figure 30). After drying, little exchange of either occurred for six days after which uptake occurred at a constant rate. Total
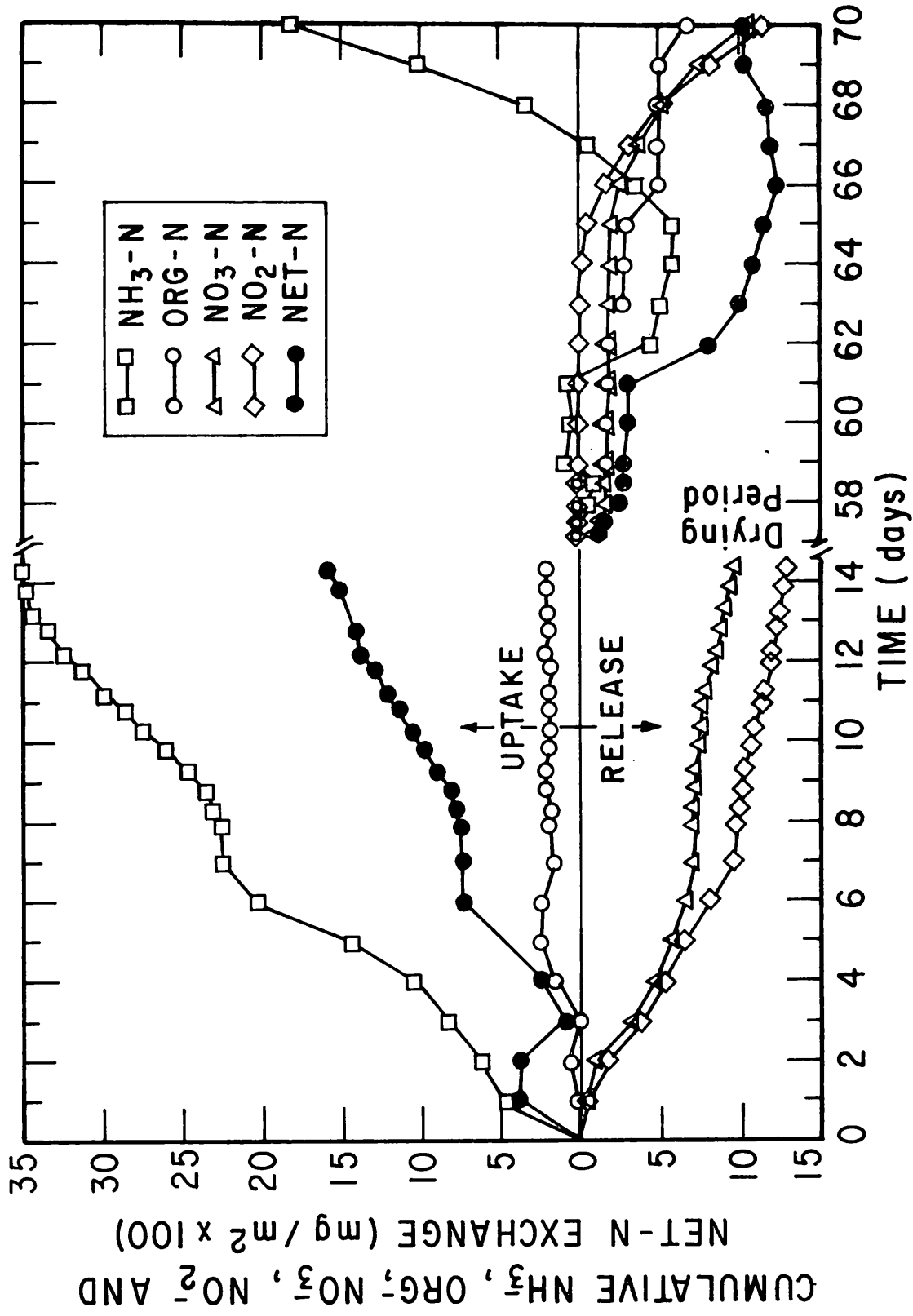
FIG. 29. CUMULATIVE NITROGEN EXCHANGE IN MICROCOSM 6 (ALGAL MAT – SPIKED)
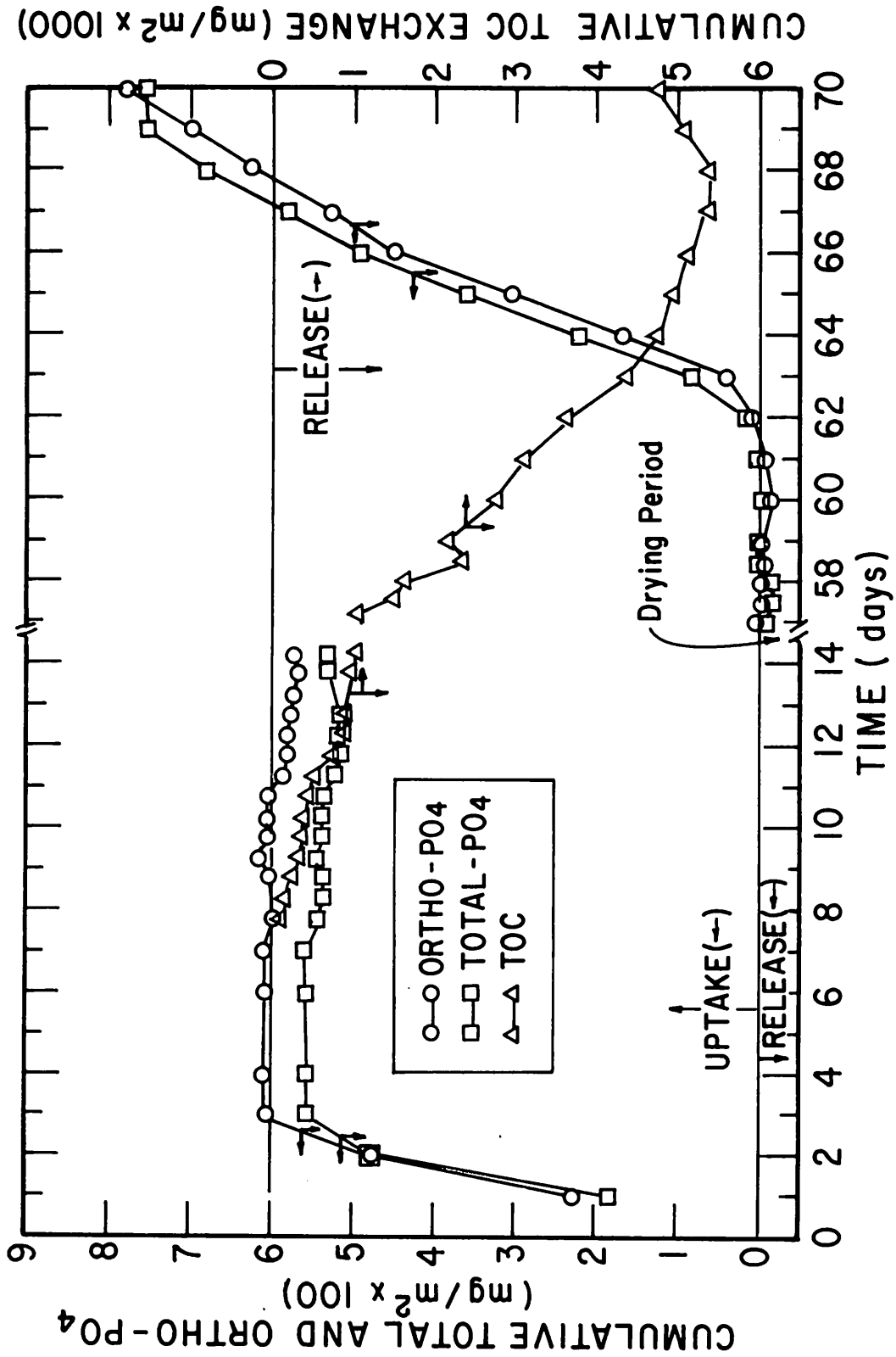
FIG. 30. CUMULATIVE CARBON AND PHOSPHORUS EXCHANGE IN MICROCOSM 6
(ALGAL MAT – SPIKED)

phosphate appeared to reach equilibrium at the end of the study.

Total organic carbon was released at a constant rate (steady state) during week two (Figure 30). After drying, it was released at a constant rate until day 67 when it appeared to approach equilibrium.

RATES OF NUTRIENT EXCHANGE

As was seen in the previous section, in most cases the rate of exchange decreased from week one to week two when the water level was lowered from four inches to one inch. As was expected, the rates of exchange of nutrients differed between microcosms. The rates also varied with the productivity of the systems as seen in the period after drying. Constant rates of release were normally achieved soon after changes in water level occurred with the exception of the reinundation period after drying. Since a majority of the plants had died during the drying period, a longer period of time was needed for the microcosms to approach steady state. The exchange rates for the microcosms are compiled in Table 6.

The increase in nitrogen and in some cases phosphorus exchange resulting from the higher concentration gradient can be easily seen by comparing the cumulative graphs for Microcosms 1 (Figures 19,20) and 2(Figures 21,22), 3(Figures 23,24) and 4 (Figures 25,26), and 5 (Figures 27,28) and 6 (Figures 29,30).

To aid in determining the comparative magnitude of the contributions of emergent vegetation, algal mat, and sediments to nutrient exchange, the mass of nutrients released or taken up by each microcosm

TABLE 6

DAILY EXCHANGE RATES OF NUTRIENTS IN BRACKISH MARSH MICROCOSMS

			Rate of Nutrient Exchange		
Microcosm	Week	Water Level (inches)	Nitrogen $(mg/m^2$-day)	Phosphorus $(mg/m^2$-day)	Carbon $(mg/m^2$-day)
1	1	4	- 37.2	- 7.8	
	2	1	- 32.3	- 5.9	-285.5
	9-10	4	-209.4	-18.9	-700.9
2	1	4	173.9	68.6	
	2	1	156.5	26.2	-159.3
	9-10	4	- 66.4	66.4	-498.5
3	1	4	24.0	- 1.4	
	2	1	2.0	- 0.2	-155.5
	9-10	4	- 11.3	0.8	-415.3
4	1	4	21.4	50.8	
	2	1	71.3	11.8	-190.8
	9-10	4	59.0	20.8	-535.6

TABLE 6 (CONTINUED)

Microcosm	Week	Water Level (inches)	Rate of Nutrient Exchange		
			Nitrogen $(mg/m^2\text{-day})$	Phosphorus $(mg/m^2\text{-day})$	Carbon $(mg/m^2\text{-day})$
5	1	4	− 71.0	−17.2	
	2	1	− 47.6	−11.3	−178.5
	9−10	4	−208.5	−19.1	−484.6
6	1	4	104.3	79.4	
	2	1	120.9	− 3.5	−150.4
	9−10	4	− 80.8	57.8	−367.8

during the various periods of the study were compiled and are presented in Table 7. The mass of nutrients exchanged was subject to the same factors that were discussed regarding the rate of exchange.

ADDITIONAL PARAMETERS

Along with analyses of nutrients, pH and temperature were monitored. The pH did not exceed 8 or fall below 6 in any microcosm. Temperature remained almost constant during the study (near $23^{\circ}C$) except during the initial thirteen days of the drying period when the heat lamps increased the temperature to as much as $40^{\circ}C$. No significant diurnal variations in nutrient exchange occurred during the second week.

SUMMARY

Communities Which Received Low Nutrient Concentrations : Reactors 1, 3, 5

In general, organic nitrogen, nitrate and nitrite were released by all of these microcosms throughout the study. During week one ammonia was taken up by the marsh grass - sediment microcosm, not exchanged in the algal mat community and was released by both for the remainder of the study. The marsh grass community took up ammonia throughout the study. Nitrate and nitrite were rarely observed in the marsh grass community. The release of nitrogen in the marsh grass - sediment reactor occurred mainly in the ammonia and organic forms. Organic release exceeded ammonia release before the drying period; the reverse was true after the drying period. This was also

TABLE 7

MASS OF NUTRIENTS EXCHANGED DURING GIVEN HYDRAULIC CONDITIONS

Microcosm	Week	Water Level (inches)	Nitrogen (mg/m^2)	Phosphorus (mg/m^2)	Carbon (mg/m^2)
1	1	4	- 260.2	- 54.37	
	2	1	- 225.7	- 41.6	-1998.4
	9-10	4	-2722.1	-245.9	-9111.7
2	1	4	1217.9	480.5	
	2	1	1095.5	183.2	-1115.3
	9-10	4	- 863.5	862.7	-6480.2
3	1	4	167.8	- 10.0	
	2	1	- 14.3	- 1.5	-1088.2
	9-10	4	- 147.1	10.8	-5398.7
4	1	4	150.2	355.5	
	2	1	499.5	83.1	-1335.5
	9-10	4	766.7	270.5	-6963.6

TABLE 7 (CONTINUED)

Microcosm	Week	Water Level (inches)	Mass of Nutrients Exchanged		
			Nitrogen (mg/m^2)	Phosphorus (mg/m^2)	Carbon (mg/m^2)
5	1	4	- 496.8	-120.2	
	2	1	- 333.6	- 78.9	-1250.0
	9-10	4	-2711.2	-248.8	-6299.9
6	1	4	730.3	556.2	
	2	1	846.6	- 24.7	-1053.0
	9-10	4	-1050.0	751.2	-4780.9

true for the algal mat microcosm, but in the algal mat system the ammonia release after drying was more than twice the organic nitrogen release whereas in the marsh grass - sediment system ammonia release exceeded organic release by only a small amount.

Phosphorus was released by the marsh grass - sediment and algal mat communities and was intermittently released and taken up by the marsh grass community.

Total organic carbon was released by all microcosms. The marsh grass - sediment and marsh grass communities released larger amounts of TOC than did the algal mat community.

Communities Which Received Additional Nutrients : Reactors 2, 4, 6

All nutrients were released during the initial period of reinundation following the drying period. Ammonia was taken up by all the microcosms with the exception of an initial release by the marsh grass system. Organic nitrogen was intermittently released and taken up. Organic nitrogen fluctuated considerably more in these systems than in those which received low concentrations of nutrients. Nitrate and nitrite were released by the marsh grass - sediment and algal mat communities and were rarely observed in the marsh grass community.

Phosphorus was taken up by the marsh grass - sediment and marsh grass systems. The algal mat reactor took up phosphorus for three days, did not exchange it for four days, then released and took it up during the second week and took up phosphorus after the initial

reinundation period.

Total organic carbon was released by all microcosms at the same
rate as in the microcosms which received low nutrient concentrations.

CHAPTER 5

DISCUSSION

INTRODUCTION

The significance of the results in regard to the pathways and the effects of drying and concentration gradients on the exchanges which occur are discussed in this chapter. Also, the results of this study are compared with those of previous studies.

MAJOR PATHWAYS OF NUTRIENT EXCHANGE WITHIN THE MARSH SYSTEM

By considering the constituents of the saltmarsh microcosms and consulting the available literature on the utilization of nutrients by these components, pathways of exchange of carbon, nitrogen, and phosphorus within the system were summarized and are presented in Figures 31, 32, and 33.

The main pathways of nutrients within the marsh system are:
1. nutrients in the sediment → macrophytes → detritus → bacteria → overlying water → export
2. nutrients in the sediment or overlying water → algae → detritus → bacteria → water → export

Additional exchanges occur between the sediments and the overlying water column. Nitrogen fixation may also occur within the marsh
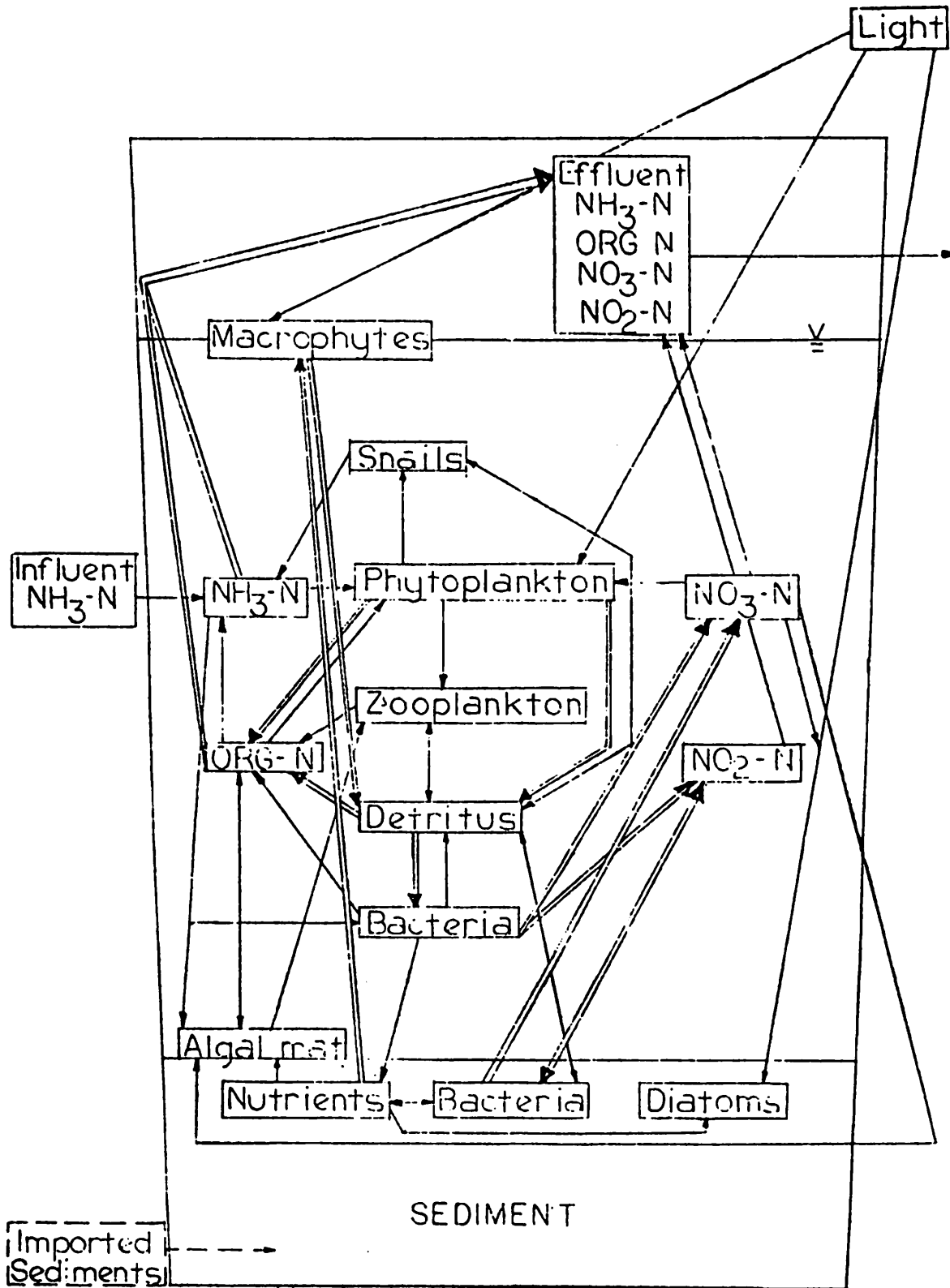
FIG. 31. PATHWAYS OF NITROGEN EXCHANGE
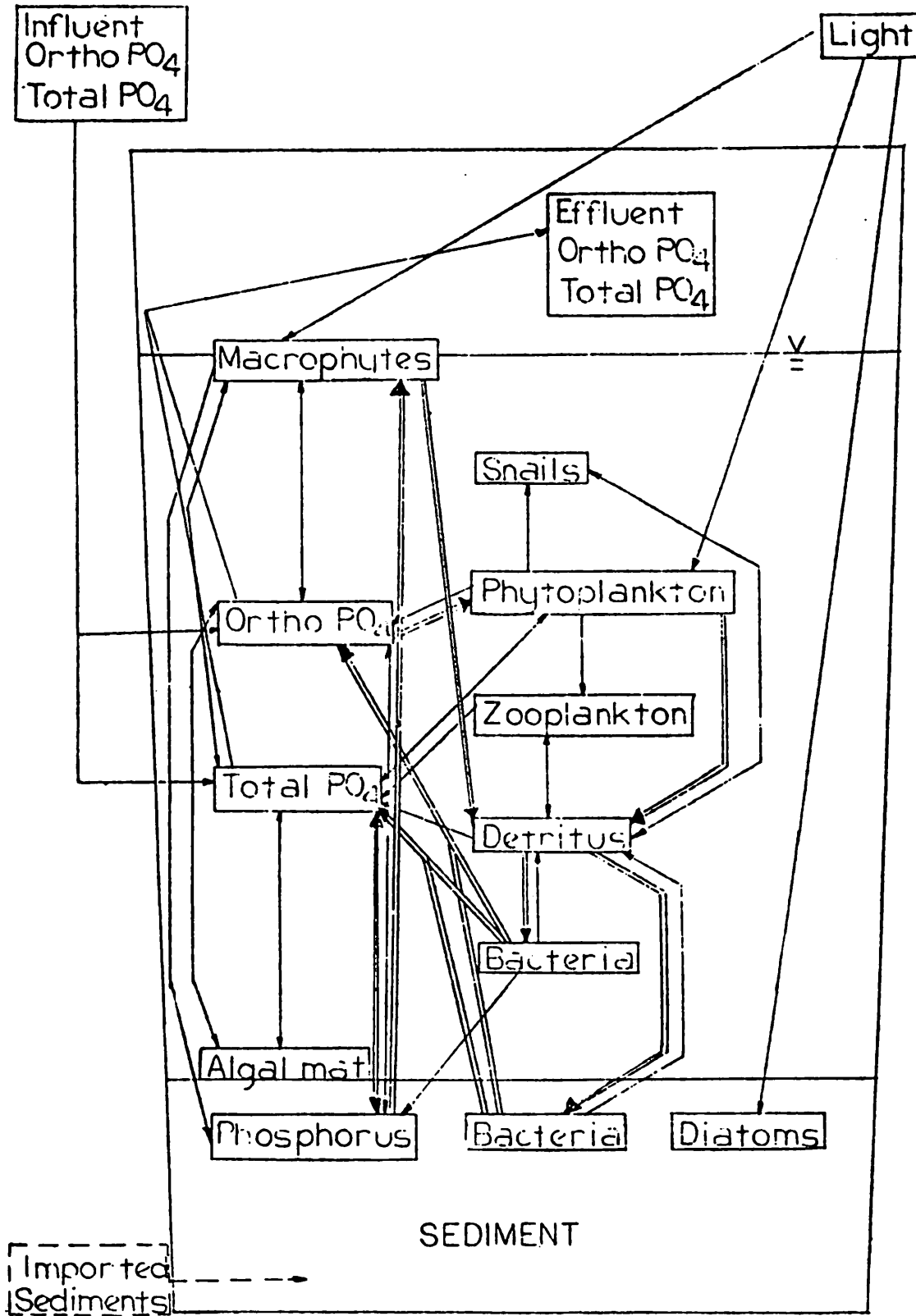
FIG.32. PATHWAYS OF PHOSPHORUS EXCHANGE
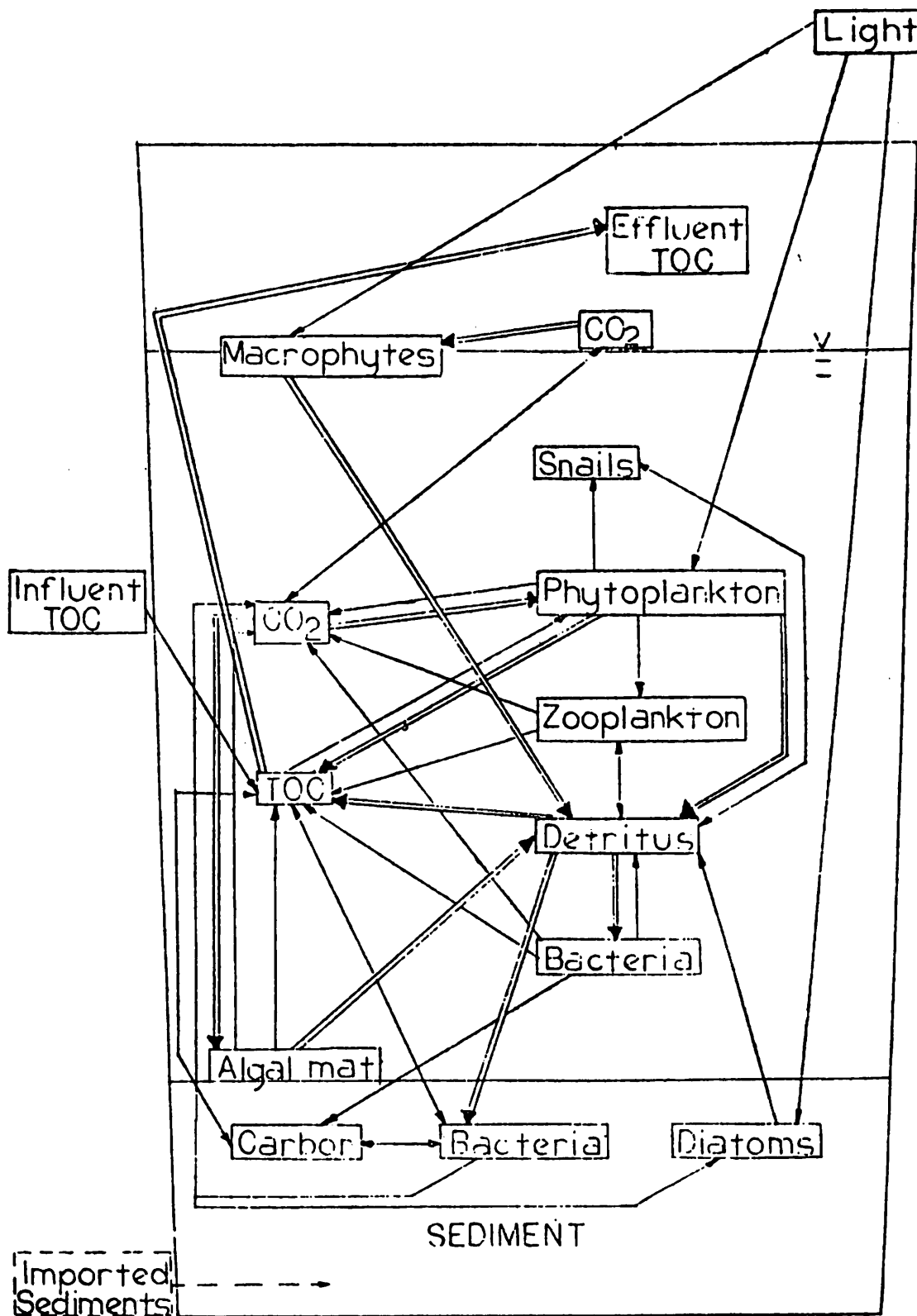
FIG. 33. PATHWAYS OF CARBON EXCHANGE

system. Other pathways of nutrient exchange in the marsh are considered to be of minor importance in comparison with these.

Nitrogen Exchange

The net flow of nitrogen out of the marsh grass - sediment and algal mat communities indicates a source of nitrogen other than the water column, presumably the sediments, indicating an exchange from the sediments to the plants. The nitrogen from the sediments may be due to either nitrogen fixation or the mineralization of materials in the sediments. In the marsh grass microcosm in which the sediments were sealed from the overlying water column, the net exchange of nitrogen fluctuated between release and uptake with ammonia-nitrogen being taken up (0.1 - 0.3 mg/l) and organic-nitrogen being released (0 - 0.2 mg/l) in varying amounts. (Ammonia nitrogen was released (0 - 0.4 mg/l) in the marsh grass - sediment microcosm as well as in the algal mat microcosm (0 - 0.2 mg/l).) It seems that the sediment - water interface is an important site of exchange and that by eliminating it, ammonia nitrogen which would otherwise be available from the sediments is unavailable. (The marsh grasses can extract phosphorus from the sediments through their roots, transport it through the plant and release it through the leaves. This may or may not occur with nitrogen in this case.) Since algae are known to utilize ammonia-nitrogen, it is possible that algae consumed the ammonia. It is also possible that the ammonia was taken up by the marsh grasses. In either case, it is apparent that nitrogen is utilized by organisms in the water column or partially submerged in it and that the source of this nitrogen is normally the sediments.

Although net exchange of nitrogen is one of release in the marsh grass - sediment and algal mat microcosms, during the first week of the study ammonia was noted to be taken up or not exchanged at all, while it was released during the remainder of the study. It may be that organisms causing a release of ammonia had not yet become well developed.

The absence of nitrate-nitrogen and nitrite-nitrogen in the marsh-grass microcosm with a layer of paraffin sealing the sediments from the water indicates that nitrification is carried on primarily by bacteria in or on the sediments. The lack of this additional nitrogen source may have been the sediment-associated factor causing an uptake of ammonia in those microcosms.

Prior to the drying period, the nitrogen released was mainly organic nitrogen. The source of this nitrogen may be either suspended organisms or the release of organic materials during decomposition.

Phosphorus Exchange

Low amounts of exchange of phosphorus were observed in all of the microcosms. The marsh grass - sediment and algal mat communities both released phosphorus. The marsh grass microcosm with paraffin released a small amount of phosphorus initially and from that time forward acted as a sink for small amounts of phosphorus. As with the nitrogen, the sediment-water interface appears to be an important site of release of phosphorus from the sediments. The plants may or may not take up phosphorus from the sediments and release it to the overlying water.

Carbon Exchange

Total organic carbon was released from all of the microcosms throughout the study. The release was greater from the marsh grass-sediment community than from the algal mat. The carbon sources in these systems are the suspended organisms and the release of organic compounds during decomposition. Since it is likely that the marsh grass - sediment system would contain a larger population of suspended organisms than the algal mat system, the difference in release may be due to suspended organisms or decomposition of plants; no differentiation was possible with the analytical techniques used, but visual observations indicated large amounts of marsh grass decomposition. This is in accord with the fact that the algae have a larger refractory portion than the marsh grasses.

The marsh grass microcosm with sealed sediments released slightly less organic carbon than did the marsh grass - sediment system. Apparently, decomposition was occurring in the water column and the sediments serve as an additional site of decomposition. That is, the sediments are a minor source of organic carbon and the plants are the primary source.

EFFECTS OF THE HIGHER CONCENTRATION GRADIENT

The large concentration gradient created by the addition of nutrients resulted in the uptake of ammonia-nitrogen by all the microcosms. This uptake of ammonia caused the net nitrogen exchange to be one of uptake. The release of nitrate-nitrogen and nitrite-nitrogen in the marsh grass - sediment and algal mat reactors

was increased simultaneously indicating an increased utilization of ammonia-nitrogen in nitrification processes.

The marsh grass - sediment microcosm took up approximately twice as much ammonia-nitrogen as the marsh grass microcosm with paraffin. Thus, approximately half of the ammonia taken up in the marsh grass - sediment system may have been absorbed by the sediment layer. This was probably either a sorption (physical) exchange or the assimilation of the nitrogen by the organisms in the sediments as implied by the increased release of nitrate-nitrogen and nitrite-nitrogen.

The increased concentration of phosphorus in the influent water caused an increase in uptake by both the marsh grass-sediment and marsh grass with paraffin reactors. The increase was in the same range in both, suggesting that the sediments were not a significant phosphorus sink despite the higher concentration gradient.

The algal mat community initially consumed higher amounts of phosphorus, then did not exchange phosphorus for several days, and finally released phosphorus within the same range as the algal mat community which received a low concentration of nutrients in the inflow water. Algae are known to concentrate phosphorus when it is available in excess amounts. The initial uptake of phosphorus by the algal mat suggests that this occurred at first. Since the marsh grass systems continued to take up phosphorus throughout the study it seems that a large portion of this excess phosphorus was utilized by the macrophytes or taken up by the sediments rather than algae. A flourishing algal community became established in the

marsh grass system with paraffin and utilized some of the excess phosphorus in that reactor. It appears that little additional phosphorus was required to sustain high algal productivity because the algae continued to fluorish when the study was completed and nutrient addition was stopped. This is in accord with the findings of Cooper (1970) in his studies of algal mat production in microecosystems of Trinity Bay.

The increased concentration gradient had no effect on the release of organic carbon.

EFFECTS OF THE DRYING PERIOD

The drying period caused an initially high release of nutrients from the microcosms upon reinstatement of flow. Ammonia-nitrogen releases occurred at this higher level for approximately a week (except in the marsh grass system with paraffin in which the release occurred for only 12 - 18 hours); nitrate-nitrogen and nitrite-nitrogen for 12 - 24 hours; organic-nitrogen for 12 - 48 hours; phosphorus for approximately 24 hours; and, carbon for 12 - 24 hours. This effect of the drying period was most apparent in the large amounts of carbon initially released. This must have been present in materials which were rapidly washed out of the system. The ammonia-nitrogen release occurred over a longer period of time than the release of the other nutrients and only occurred in the marsh grass - sediment and algal mat communities suggesting a slow release of ammonia from the sediments. The ammonia may have been held in interstitial water which exchanged slowly with the overlying water or may have been held by clay particles. The release of ammonia-nitrogen after the drying

period exceeded that of organic nitrogen in the marsh grass - sediment microcosm by a small amount and was more than twice that of the organic nitrogen released from the algal mat community. Apparently, a greater amount of ammonia was released from algal decomposition than from decomposition of marsh grasses during the dry period.

The additional nutrients in the marsh grass - sediment microcosm caused phosphorus to be taken up rather than released. In the marsh grass - paraffin microcosm the additional nutrients caused increased release of orthophosphate and release rather than uptake (as occurred with low nutrient concentrations) of total phosphorus. In the algal mat microcosm receiving additional nutrients there was an initial uptake of phosphorus (did not occur in algal mat microcosm receiving low nutrient concentrations) followed by release at a lower rate prior to drying than occurred with low nutrient concentrations. Both algal mat communities exchanged phosphorus in approximately the same manner after drying.

Additional nutrient concentrations did not appear to have any effect on the release of total organic carbon.

Due to the nature of the studies, it is not possible to determine whether these initially high releases compensate for the lack of release during the period when the marsh is dry.

COMPARISON WITH PREVIOUS STUDIES

The results of this study compare favorably with those of the study of the same area of Lavaca Bay by Armstrong et al. (1975).

The levels of nitrogen and carbon released from the marsh area are similar to those released from the microcosms. Little phosphorus exchange was noted in either study. These low amounts of phosphorus also concur with the findings of Bruce and Hood (1962) in their study of Texas Bays. In the field studies by Armstrong et al. (1975) as well as in microcosm studies done at that time results indicated an uptake of phosphorus by the salt marsh. In contrast, evidence from this study indicates a release of phosphorus from the marsh system. In addition, in the previous marsh reactor studies, nitrate-nitrogen and nitrite-nitrogen were lost to the system whereas in this study there was an apparent release of these nitrogen forms. This is probably due to physical differences between the two microcosm studies such as temperature or concentrations of nutrients in the influent water.

The release of organic nitrogen exceeded that of ammonia-nitrogen in the previous field studies. This was found to be true in this study only prior to the drying period. Afterwards, the ammonia release was greater. This situation may reverse itself with time but did not do so during the two weeks of the study after the drying period.

The previous study (Armstrong et al., 1975) resulted in the conclusion that the marsh acts as a source of nutrients for the surrounding area and the results of this study firmly support that conclusion.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The analysis of the results of this study lead to the following conclusions:

1. The exchange rates of nutrients varied with changes in water level as seen in the cumulative mass graphs. The higher concentration gradient (in microcosms with additional nutrients in the influent flow) caused higher exchange rates of nitrogen and, in some cases, phosphorus but did not affect total organic carbon release.

2. Periods of drying during the summer cause an abnormally high release of nutrients when flows initially reinundate the area due to the sloughing off of detrital material which had accumulated, the release of accumulated products of decomposition, and the apparent lack of nutrient demand at normal levels by the marsh grasses and algae since the populations had been greatly decreased by the drying process.

3. During periods of normal inundation, algal mat communities release a greater amount of phosphorus and nitrogen than do marsh grass communities. The release of total organic carbon, however, is greater from the marsh grass communities.

4. The release of nitrogen from the marsh system occurs mainly in organic nitrogen and ammonia-nitrogen forms and is likely

to be primarily the result of decomposition. Export of total organic carbon is also attributed primarily to the products of decomposition.

5. The sediments are an important source of nitrogen and phosphorus in the salt marsh system and also serve as the primary area in which nitrification occurs.

6. The saltmarsh system exports nitrogen, phosphorus and carbon to the surrounding waters via the tides enabling estuarine areas to be considerably more productive than adjacent areas.

RECOMMENDATIONS

There are several additions which could be made to this study:

1. Replicates of microcosms could be utilized to provide the necessary data for error analysis.

2. By measuring the amount of nutrients in the sediment before and after experiments are conducted, the amount of uptake or release by the sediment could be determined. In addition, a comparison of these results for the marsh grass microcosm with sediment and the marsh grass microcosm with a paraffin layer sealing the sediment from the overlying water, could determine whether or not nitrogen fixation occurs in the sediment.

3. Similarly, a measurement of the standing crop and nutrient content of the macrophytes and algae before and after experiments are conducted would enable the determination of the amount of uptake or release by these components of the marsh system.

4. Nutrient tracers in the influent flow could be utilized to determine the amounts and directions of exchanges occurring between the water column and the major components of the marsh system (macrophytes, algae, sediment).

5. Further analysis of the data could be done. A statistical analysis would enable the determination of the significance of the results. Since several of the graphs indicate a linear response with time, a kinetic approach could also be used in further analysis, thus enabling a determination of the mechanisms of the nutrient exchanges which occurred in the microcosms.

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PART III:

THE ROLE OF SEDIMENTS IN NUTRIENT EXCHANGE
IN THE LAVACA BAY BRACKISH MARSH SYSTEM

by

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December 31, 1976

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CHAPTER I

INTRODUCTION

NEED FOR THE STUDY

The brackish water marshes associated with many Texas estuaries store nutrients in large amounts as they become trapped within the marsh through buildup of sediments. These sediment deposits accumulate in the estuarine systems in appreciable quantities, primarily when seasonal river flood flows occur. Soil nutrients in marshy areas are thus accumulated, used by marsh plants and microorganisms, stored in the biomass of the marsh flora and the sediment for use in later seasons. The storage and release of nutrients used by plants and animals living in brackish marshes must be understood in order to properly plan for the development of the source streams which feed the bays and marshes.

The biological cycling of nutrients, mainly nitrogen and phosphorus, in marshes has been the subject of numerous investigations and studies, particularly along the Atlantic coast of the United States. Marsh productivity, pathways of nutrients, and the generation of detritus have been studied in detail. However, studies of Texas marshes have been neglected with regard to their contributions of inorganic nutrients and organic materials to estuarine systems.

It is fundamental that a sufficient nutrient supply is necessary for the maintenance of maximum production in any biological system. This is usually accomplished in natural systems by the recycling of nutrients released during the respiration of consumers and decomposers. In Texas bays, three types of systems yield nutrient levels sufficient for high productivity. These are: (1) hypersaline regimes, (2) bottom grass-algal systems, and (3) systems receiving nutrient enriched waters. In hypersaline bays which are stable with little flushing, higher

productivity occurs; these bays are believed to be nutrient self-regenerating. In bottom grass-algal areas where flushing action is minimal, the bottom system conserves nutrients for sustained high production. In areas with high-transport inflow of nutrients, flushing may not diminish nutrient supplies (Odum, et al., 1962). As part of the bay systems noted above, the marsh area contributes to the estuarine nutrient supply and nutrient cycle.

The Texas Water Development Board is developing a mathematical model of the Lavaca River, Lavaca Bay, and Matagorda Bay system. This model will be used to determine what effects development of the river and its streams would have on future productivity of this system in particular and Texas baysystems in general. While assembling data for this model, however, the Board found that information was lacking on the concentrations of nutrients imported by rivers and from biogeochemical cycles of carbon, nitrogen and phosphorus in the marshes. To identify nutrient pathways and the possible role of sediments as a temporary storage site for nutrients, the estimation of nutrient exchange rates between sediment and water became of paramount importance. To provide these data, the Center for Research in Water Resources, University of Texas at Austin, supported by contracts with the Board, began field and laboratory investigations in 1974. This study is a portion of this overall contract.

PURPOSE

The purpose of this research was to determine the rates of release and uptake of nitrogen and phosphorus by sediments of the Lavaca Bay brackish marsh system and the effects of temperature and salinity on these rates.

SCOPE

To achieve the principal objectives of determining the release and uptake rates of nitrogen and phosphorus from marsh sediments and the effects of environmental variables on those rates, the scope of this

project required investigation of the relationship between temperature, salinity, and nutrient exchange rates. These exchange rates had been investigated earlier using fixed-bed, static, reactor systems by continuously adding varied amounts of nitrogen and phosphorus to the system and monitoring the uptake into the sediments until equilibrium conditions were attained (Armstrong, et al., 1975). The nutrient uptake phase was followed by monitoring the release of nutrients from the sediments. Results from the previous project indicated that uptake and release (leaching) of nutrients from sediments in the fixed-bed cores should be carried out in constantly stirred, flow-through reactors to arrive at rate data.

This project was carried out in the laboratory and was designed to provide comparable rates of release and uptake under varied temperature and salinity conditions. Fixed-bed reactors containing cores of marsh sediment were collected and operated as completely-mixed, flow-through reactors.

As part of this overall project, another investigation using larger portions of the marsh and involving nutrient exchange between the waters and the marsh grass, algal mat, and sediment was carried out (Dawson, 1975).

ACKNOWLEDGEMENTS

CHAPTER II
LITERATURE REVIEW

INTRODUCTION

Much work has been performed in the past to identify to what extent river, lake, and estuarine sediments affect nutrient concentrations of the overlying waters and to identify and confirm the roles of nitrogen and phosphorus as the controlling nutrients for production rates in these waters. In this chapter this literature and especially that pertinent to brackish water areas is reviewed.

NUTRIENT-SEDIMENT EXCHANGE STUDIES

Introduction

The literature review was carried out in four primary areas:
(1) general nutrient exchange studies; (2) nitrogen exchange; (3) phosphorus exchange; and (4) effects of environmental conditions on exchange rates. Most of these have dealt with the uptake and release of phosphorus as a limiting nutrient. However, in recent years, nitrogen exchange with sediments has received much attention. The publications cited and reviewed in this chapter cover some of the literature bearing on this subject.

General Nutrient Exchange

The pathways of nutrients from fresh water into brackish waters are complex and somewhat speculative. One of the primary paths for nutrient transport into a marsh is with the stream flow; the nutrients are attached to suspended sediments, or are in the soluble form. Following flocculation of colloids and deposition of sediments in brackish marshes, the exchange of nutrients becomes a constant renewal and depletion process. Gardner (1975) investigated the runoff from marsh areas during tidal exposure and found it rich in dissolved silica, phosphate, bicarbonate and probably

ammonia. He concluded that nutrient diffusion from the active sediment layer was the major mechanism by which nutrients are transferred to the overlying water during low tide, while upward seepage of marsh water through the sediments during high tide was relatively minor. His analysis was based on numerous interstitial water samples collected from creek banks and interior areas of the marsh, and it appeared that the enrichment pattern was the result of slow drainage from puddles on the marsh flats into the channel system. He also found that marsh runoff contained much higher nutrient concentrations than fresh waters entering the marsh.

Abbott (1967) investigated the "spill situation" discharge of a single nutrient into receiving waters, observing luxuriant algal blooms comparable to those occurring under sewage pollution conditions. In his experiments microcosms were used, and they became autotrophic and aerobic for up to twenty-five weeks. Jewell (1971) and Teal (1962) pointed out that the major sources of natural organic materials in marsh systems are emergent plants and phytoplankton. They also showed that nutrients are released during decay and that plants supported an abundance of aquatic animal life in estuaries because tides remove up to forty-five percent of the production to the adjacent waters before the terrestrial marsh consumers have a chance to use it.

Fillos (1972) investigated the mechanism of long-term nutrient release from benthal sediments under both aerobic and anaerobic conditions. Results indicated, as other investigators had suggested before, that aerobic and anaerobic bacterial activity seemed to be contained mostly in the upper ten centimeters of bottom deposits. He also confirmed that benthal deposits create a dissolved oxygen sink and an immediate oxygen demand for the reduced substances such as ferrous and sulfide ions coming from the anaerobic layers. He found, moreover, that benthal deposits release organic materials and various nutrients to the overlying waters. These released nutrients in turn promote considerable biotic growth. Fillos (1972) then concluded that in any water quality management program the sediments must be considered as intermittent sources of nutrients as well as a continuous sink for dissolved oxygen.

Porcella et al. (1970) commented that, although chemical and physical factors affect nutrient equilibria, biota also have a significant effect. He pointed out that biological effects cannot easily be separated from the physical and chemical relationships which control the availability of nutrients since increased nutrient concentrations can lead to increased biomass and thus increased use of nutrients.

Nitrogen Exchange

Available literature on the movement of nitrogen in waters and sediments was reviewed by Keeney (1973) with emphasis on the importance of nitrogen to aquatic productivity, the pathways leading to nitrogen gains or losses in aquatic ecosystems and the availability of nitrogen in sediments to overlying waters. He noted that the nitrogen cycle in sediment and water systems is more complex than in terrestrial systems. A much simplified diagram of the sediment and water nitrogen cycle is shown in Figure II-1 as a guide to the following discussions.

Forms of Production

The dominant species of nitrogen in waters are ammonia, nitrite, nitrate, dissolved and particulate organic nitrogen. The concentrations of the various nitrogen species in water is the net result of nitrogen deamination, hydrolysis, nitrification and denitrification. Several investigators, including Copeland and Fruh (1970), Keeney (1973), and Ryther and Dunstan (1971) quote accumulating evidence that nitrogen rather than phosphorus may be the limiting nutrient for algal growth in coastal waters, especially where large amounts of available phosphorus remain within the sediments and are released slowly over long periods. Evidence also indicates that algae use primarily inorganic forms of nitrogen and that ammonia may be used preferentially (Syrett, 1962). Nitrogen in sediments is present largely as organic nitrogen. In general, the total nitrogen contents of surface sediments ranged from one-tenth percent to as high as four percent nitrogen (Keeney et al., 1970).

FIGURE II-1

THE NITROGEN CYCLE IN SEDIMENTS AND WATERS, AFTER KEENEY (1973).
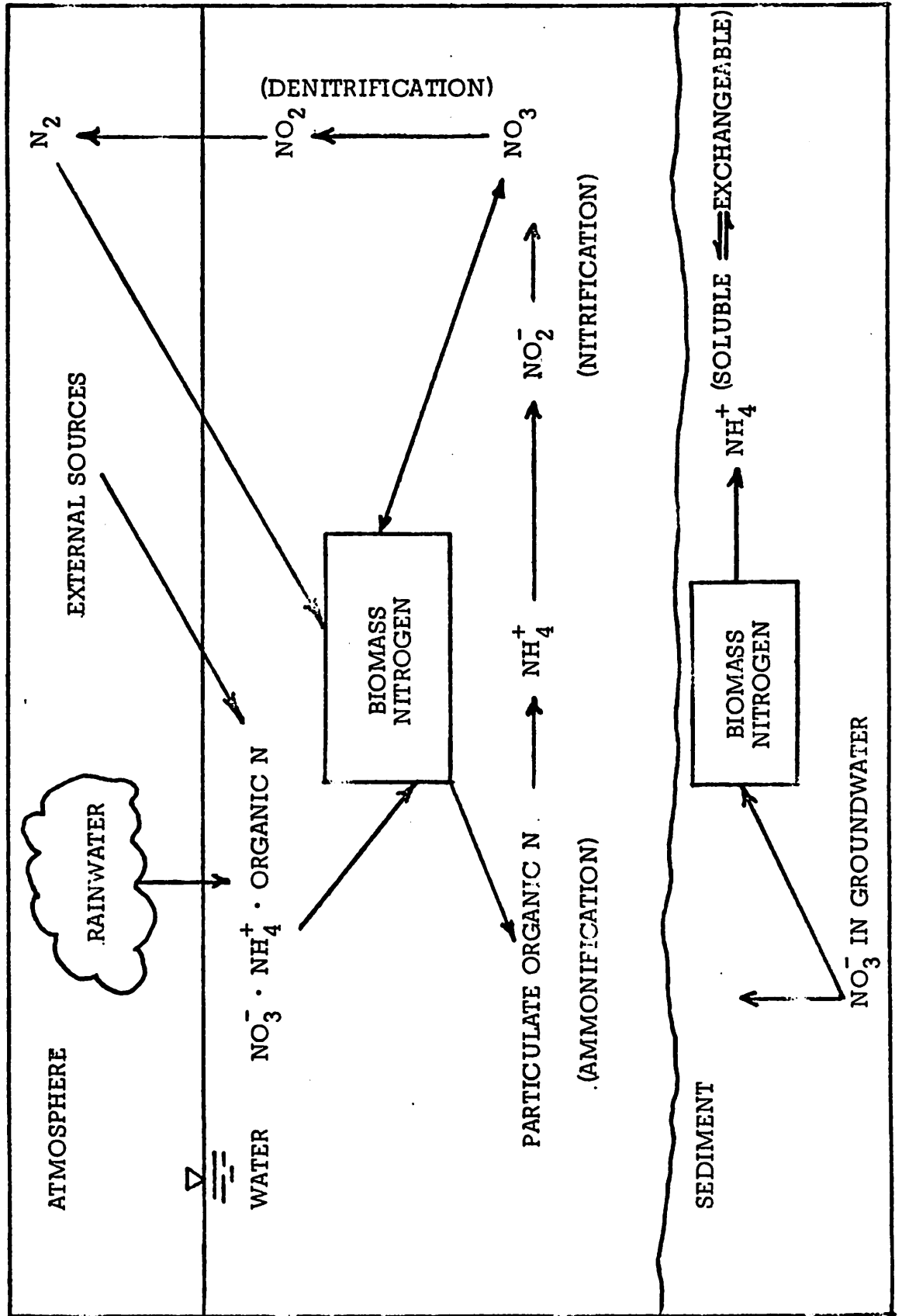
Assimilation and Release

Assimilation, or the incorporation of molecular nitrogen, ammonia, nitrate, or organic nitrogen in living biomass, is a necessary life process. The reverse (release or mineralization) processes are occurring simultaneously in most systems, and the net change in nitrogen is reflected in the biomass level of nitrogen at any given time (Keeney, 1973). Another dominant factor, especially for heterotrophic bacteria, is the available energy in organic material. If excess energy material is present, available nitrogen will be utilized until the C:N ratio is in favor of the net mineralization of nitrogen; and, conversely, if nitrogen rich residues are being decomposed, inorganic nitrogen is released to the waters. Nitrogen is also excreted by aquatic animals as ammonia, free amino acids, and other organic compounds which are then available for use by phytoplankton and bacteria. Detritus is also decomposed through bacterial action, and from twenty-five to seventy-five percent of the nutrients are released rapidly. Temperature will also markedly influence regeneration, turnover, and assimilation processes. Increasing temperature increases biochemical processes, but it is generally concluded that, at least in terrestrial systems, higher temperatures favor decomposition over assimilation because microbial activity rates at lower temperatures decrease more rapidly than does the photosynthetic rates of plants (Senstius, 1958). It is assumed that the reverse occurs with increasing temperatures in aquatic systems.

Environmental variables play a key role in the assimilation-release-ammonification processes. The decay of nitrogenous organic matter with the production of ammonia or ammonium compounds (especially by the action of bacteria) is ammonification. Ammonification proceeds at a measurable rate at low temperatures when assimilation is usually low. Under anoxic conditions, net mineralization of nitrogen is characteristically greater than under aerated conditions, due to the lower efficiency of converting organic carbon to cell carbon by heterotrophic anaerobes compared to the high efficiency of autotrophic aerobes.

Nitrification

Nitrification is defined as the biological conversion of nitrogen in organic or inorganic compounds from a reduced or partially oxidized state to a more oxidized state. Nitrification refers to the biological oxidation (needing only carbon dioxide or carbonates as a source of carbon) of ammonia to nitrate with ammonium hydroxide and nitrite as intermediates with the net reaction being

$$NH_4^+ + 2 O_2 \longrightarrow NO_3^- + H_2O + 2H^+.$$
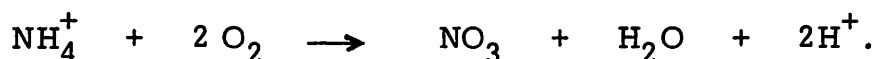
Nitrification is a key process affecting the nitrogen budget and productivity in aquatic ecosystems. Because preferential uptake of nitrate over ammonia (and vice versa) occurs among various algae, the presence of nitrate has a great influence on the productivity of the water system. Also nitrate formed in hypolymnetic waters and at the sediment-water interface is subject to denitrification during anoxic conditions following density stratification. Recent investigations by Chen et al. (1972a) showed that nitrification occurred rapidly in well-buffered calcareous sediment interstitial waters when well-stirred such as in shallow waters. Nitrification rates were much lower for unbuffered sediments (those formed under acidic conditions and not containing $CaCO_3$). On the other hand, under quiescent conditions (compared to well-stirred conditions) much less nitrate accumulated while ammonia decreased indicating that nitrification, nitrate assimilation, and denitrification occurred at the same time. The nitrate which was produced in the upper sediment layer was being immediately denitrified or immobilized adjacent to the oxidized zone in the anaerobic zone. This indiciated that sediments do not add nitrate to water except in well-oxidized, well-stirred situations, such as might occur in shallow waters or at lake turnover. Chen et al. (1972a) showed that nitrification rates in sediment-water systems showed a doubling with each $10^\circ C$ increase in temperature. A temperature increase of $15^\circ C$ increased the nitrification rate 2.7 times.

Denitrification

Denitrification is defined as the biochemical reduction of nitrate or nitrite to gases (molecular N_2 or nitrogen oxides). Microorganisms may reduce nitrate to protoplasm (assimilatory reduction) or to gaseous nitrogen compounds (denitrification). Several investigations have confirmed that the sequence

$$NO_3^- \longrightarrow NO_2^- \longrightarrow N_2O \longrightarrow N_2$$
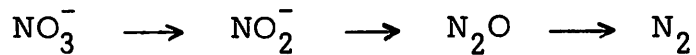
represents true biochemical denitrification and will occur in any microbial environment that is essentially anaerobic. Water stagnation or any means of limiting oxygen diffusion, coupled with oxidizable substrate allows denitrification to occur.

Numerous investigations have shown the rate of denitrification in submerged soils is related to the organic matter content. The rate of denitrification is influenced by pH, being lower in acid than neutral or alkaline systems. It is also influenced by temperature with the optimum rate at $60\text{-}65^\circ C$ and slow rates at lower temperatures (Bremner et al.,1958).

Recent work by Chen et al. (1972b) has shown that in lake sediments, assimilatory nitrate reduction and denitrification occur at the same time. Chen et al. (1972c) indicated that denitrification is a significant nitrogen sink in lakes. In their work, nitrate added to sediments disappeared rapidly from lake sediments; within two hours up to 90 percent of added nitrate injected under the sediment surface disappeared from a 100 ml sample of Lake Mendota sediment.

Nitrogen Fixation

Until recently, the aerobic blue-green algae were believed to be the significant nitrogen-fixing organisms in water. However, evidence of nitrogen fixation in anoxic waters and sediments, presumably by anaerobic heterotrophs, has been reported (Chen et al., 1972c). The authors indicate that nitrogen fixation in sediments might be significant. The hypothesis

is that some of the nitrogen gas formed in denitrification is subsequently fixed by bacteria. The significance of nitrogen fixation to the nitrogen economy of lakes is as yet largely unknown. In general nitrogen-fixing algae appear to be more prominent in eutrophic lakes, especially those high in phosphorus (Sawyer and Ferrulo, 1960). The present opinion is that blue-green algae are the dominant nitrogen fixers in surface waters, with bacteria playing an insignificant role (Kuznetsov, 1968). Nitrogen fixation rates in estuarine sediments are usually low and probably of minor importance to nitrogen budgets of waters, but the process possibly has important biogeochemical implications (Keeney, 1973).

Role of Sediments

Physical, chemical, and biological processes are involved in determining the net uptake or release of nutrients and other materials at the sediment-water interface. These are often interrelated, and the overall process of sediment-water interchange is complex. An understanding of these processes is needed to evaluate the role of estuarine sediments in estuarine production and to properly evaluate laboratory results simulating in situ conditions.

Austin and Lee (1973) found that biochemical and physiochemical activity can release nitrogen from sediments in the form of ammonium which accumulates under anaerobic conditions but will be oxidized to nitrate under aerobic conditions. Both forms are then usable by algae in primary production. This study showed that a substantial fraction of nitrogen compounds can be released from the sediments under completely mixed aerobic conditions. It was proposed that one of the primary reasons lake sediments act as a nitrogen sink is because of the relatively poor mixing which occurs within the overlying waters. Shallow waters with greater mixing promote organic nitrogen solubilization and mineralization which results in a relatively low concentration of organic nitrogen in the sample.

A working model for nitrogen uptake or release by sediments must include the processes that control the nitrogen content of the interstitial

water and the release of nitrogen from the interstitial water to the over-lying waters. The model presented by Keeney (1973) (see Figure II-2) is simple but illustrates the interrelated complexities involved. The historical (unmixed) sediments are overlain by a homogeneous layer of active sediments several centimeters thick which is constantly reworked by physical and biological processes. This active sediment remains relatively constant in thickness, and layers of historical sediment accumulate at a rate dependent on the sedimentation rate.

Lee (1970) regards hydrodynamic effects to be the rate-controlling step in exchange reactions. Included are wind-induced gradient currents and hydraulic head which transport released materials from the sediment-water interface allowing concentration-dependent exchange reactions to proceed towards re-establishing equilibrium. He cites results from his investigations indicating that the depth of mixing into the sediments is on the order of five to twenty centimeters, a conclusion that has been confirmed by other investigators (Davis, 1968; Hynes and Greib, 1970; Veith and Lee, 1971). Mixing of sediments is generally attributed to activities of benthic organisms, rough fish, gases, and wind-induced currents.

Microbiological reactions play an important role in sediment-water exchange of nitrogen. Besides the obvious mineralization-immobilization and denitrification processes, microbes also exert several indirect effects. These include alteration of pH and oxidation-reduction levels, consumption of oxygen, production of gases, and formation of soluble cations which may compete for ammonia on the soil exchange sites as interstitial water ammonia is depleted. Clays and other inorganic colloids readily sorb organic nitrogenous compounds. Sorption of soluble organics by sediment particles controls their future release to interstitial waters and probably retards decomposition by biochemical reactions. Other losses of nitrogen in association with sediments include: loss of nitrite in nitrification and loss of ammonia in alkaline waters (pH greater than 8.5 to 9) by volatilization from surface layers (Straton, 1969).

FIGURE II-2

A SEDIMENT-WATER INTERCHANGE MODEL, AFTER KEENEY (1973).
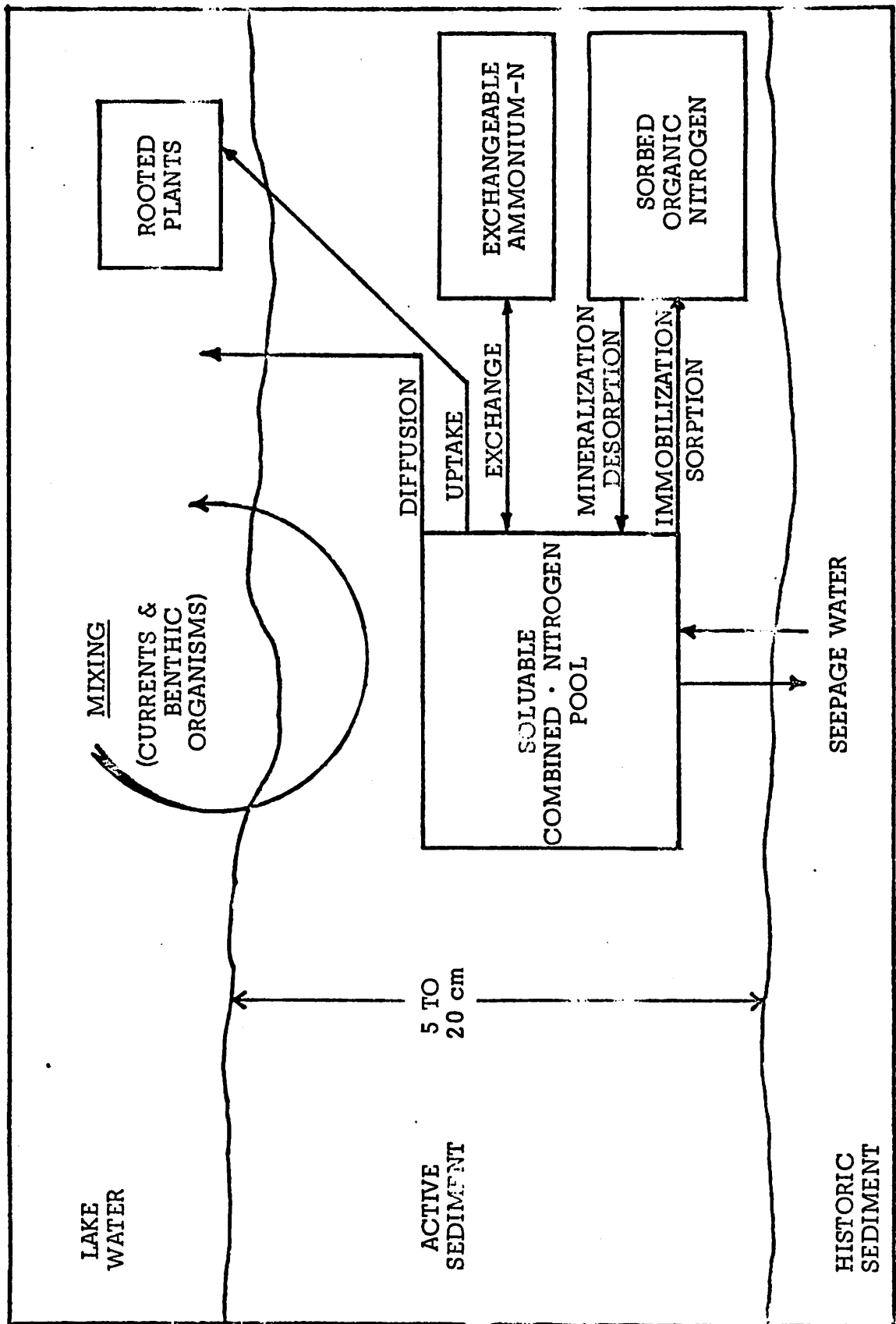
Phosphorus Exchange

Role of Phosphorus

Phosphorus is an essential element in the formation of protein and is considered a major nutrient. Phosphorus exists in soluble and insoluble forms and has several pathways between sediment and water. The general interactions of phosphorus can be represented schematically in terms of a sediment-water system (see Figure II-3). Porcella et al. (1970) discussed the forms of phosphorus as minerals in sediments, as solute in interstitial waters, and as organic phosphorus. The availability of soluble orthophosphate (usable form by plants and microorganisms) in overlying waters in a sterile environment is dependent upon complex chemical, biochemical, and physical reactions. They noted that in natural ecosystems growing life forms affect mixing, translocation of sediments, gas production, and alteration of chemical conditions which may overshadow the non-biological reactions. Productivity may be increased through greater phosphorus solubilization than would be expected from a pure non-biological reaction. They also suggest the possibility that organic materials would increase the release of phosphorus from sediments by serving as substrate for anaerobic bacteria that would in turn lower the sediment pH and increase phosphorus solubilization.

Mechanisms of Phosphorus Exchange

Syers et al. (1973) considered dissolved inorganic phosphorus in sediment interstitial waters completely mobile, whereas inorganic phosphorus sorbed onto sediment in equilibrium with inorganic phosphorus in solution was potentially mobile. Inorganic phosphorus exists in two general forms: (1) phosphorus within discrete phosphorus compounds such as apatite $Ca\,FCa_4(PO_4)_3$; and (2) phosphorus sorbed onto sediment surfaces or present within the matrices of iron, aluminum, or calcium component of sediments. They state that the mobility of phosphorus in these discrete compounds is predicted by solubility product relationships and is mainly influenced by ionic concentrations in solution and by pH.

FIGURE II-3

A PHOSPHORUS CYCLE IN SEDIMENTS AND WATERS
(After Syers, et al., 1973)
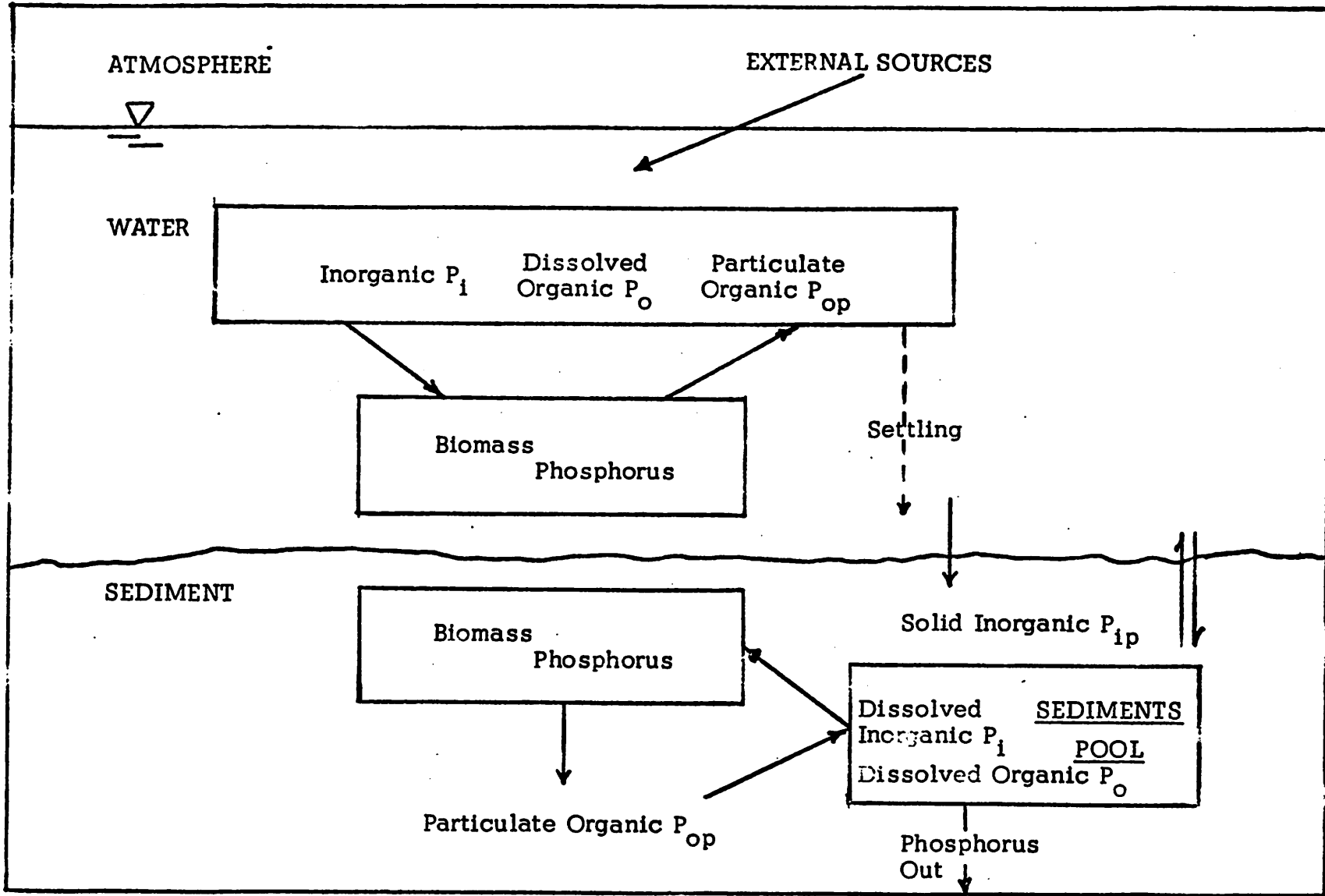
Recent work by Lee (1970) has shown that release of dissolved inorganic phosphorus can occur under aerobic conditions, although the rate of release was significantly slower than under anaerobic conditions. Whether this release under aerobic conditions is due to desorption is uncertain. Adsorption involves a process in which there is a tendency for the free energy of a solid surface to decrease, which results in the accumulation on the solid surface of some constituent at a greater concentration than exists at a distance from the surface. Absorption is the process by which solids take up a portion of a solution (much the same as a sponge soaking up water). Carritt and Goodgal (1954) examined the phosphate-solids exchange system of Chesapeake Bay sediments using a slurry system and suggested that exchange might by of ecological importance because of the quantity of phosphate sorbed per unit weight of sediment, the reversible nature of the reaction, and the variations in the amount of phosphate sorbed under different conditions of pH, temperature, salinity, and phosphate concentration. The effect of pH on the uptake of phosphorus was measured in the range of pH 2 to 10. For a contact time of 21 hours, at a pH of 4.5 peak of 85 percent phosphorus was sorbed while only 24 percent of phosphorus was sorbed at a pH of 8.5. The effect of temperature on sorption was measured by following uptake of phosphorus at 0°, 23°, and $50^{\circ}C$. After two hours exposure, the results showed sorption of less than 10 percent of phosphorus at $0^{\circ}C$, 30 percent of phosphorus at $23^{\circ}C$, and 55 percent of phosphorus at $50^{\circ}C$. The uptake of phosphorus was measured for sea water systems with salinities of 17 and 34 ppt. Removal of phosphorus from solution was found to be less in sea water than in fresh water systems although reduction in uptake was not in direct proportion to the salinity. This was thought to be attributable to the agglomeration of solids, noted especially at 34 ppt salinity. The effects of salinity on uptake of phosphorus at the end of two hours were reported as 55 percent for 0 ppt, 28 percent for 17 ppt, and 23 percent for 34 ppt salinity. The effects of variations in pH, temperature, and salinity were neglected in treatment of field date by Carritt and Goodgal (1954), since no convenient way of measuring them in the field could be found at that time. Their results were inconclusive in obtaining a measurable phosphate-solids sorption reaction.

Role of Sediments

Total phosphorus levels in sediments are determined by the levels of inorganic and organic phosphorus which are probably controlled by largely independent factors (Williams et al., 1971c). Inorganic phosphorus frequently constitutes the major portion of the total phosphorus in sediments.

Sorption and Desorption: The ability of sediments to sorb inorganic phosphorus added in the laboratory has been studied in recent years with a view of understanding the role of sediments in the removal of dissolved phosphorus from, or the release of dissolved phosphorus to interstitial waters. Laboratory studies have shown that inorganic phosphorus, added at concentrations considerably greater than those present in the interstitial waters of sediments, is retained by oxides and hydrous oxides of iron and aluminum (Muljadi et al., 1966) and $CaCO_3$ (Cole et al., 1953) by sorption rather than a precipitation mechanism. It may be expected that similar sorption mechanisms are responsible for the removal of inorganic phosphorus from solution in sediment-water systems. The extensive and rapid exchange of inorganic phosphorus between the solid and solution phases (Hayes and Phillips, 1958) provides further evidence of a sorption rather than a precipitation reaction. In general, high phosphate adsorption by clays is favored by a lower pH. Maximum sorption of orthophosphate on montmorillonite occurs at pH 5-6. Sorption by kaolinite is maximum at a pH near 3. Sediments are frequently able to sorb large amounts of added inorganic phosphorus (Carritt and Goodgal, 1954). Although this suggests that many sediments are not saturated with inorganic phosphorus, it is important to recognize that the levels of dissolved inorganic phosphorus sustained by the solid phase at high levels of phosphorus addition are usually considerably greater than those which exist in the interstitial waters of sediments.

Sorption studies have shown that some sediments, for example those from Lake Wingra (a eutrophic lake in Wisconsin), are virtually saturated with inorganic phosphorus (Williams et al., 1970). An inverse relationship has been reported (Williams et al., 1970) between the amount of

added inorganic phosphorus sorbed and that desorbed in a subsequent desorption step. The laboratory studies reported by Shukla et al. (1971) indicate that the ability of a sediment to sorb inorganic phosphorus added in the laboratory is closely related to the level of native inorganic phosphorus which accumulates in the sediment in the lake environment. The adsorption isotherms of phosphate have been determined (Muljadi et al., 1966) at pH 5 on potassium phosphate using three types of clays at 2°, 20°, and $40^{\circ}C$. The extent of adsorption increased with temperature largely because of an irreversible increase in the number of adsorption sites. Adsorption is usually exothermic, leading to a decrease in adsorption increase in temperature. This did not follow for the sorption of phosphate. The level of dissolved inorganic phosphorus in the interstitial water of sediments should be controlled by sorption and desorption reactions. It may be expected that surficial sediments which are nearly saturated with inorganic phosphorus are more likely to release inorganic phosphorus to the overlying water. The fact that there was no obvious relationship between the ability of a sediment to sorb added inorganic phosphorus and the trophic state of the lake (Williams et al., 1970) demonstrates the complexity of the factors controlling eutrophication.

Mobility Of Inorganic Phosphorus: Chemical mobility is a function of the rate and extent of sediment inorganic phosphorus interactions with the surrounding water and is determined by the forms of sediment inorganic phosphorus. Chemical mobility prediction and evaluation are based on the forms of sediment inorganic phosphorus, the sorption and desorption of inorganic phosphorus by sediments, and measurements of inorganic phosphorus exchanged between the solution and sediment phases, using ^{32}P-labeled phosphate. Early experiments demonstrated the occurrence of phosphorus exchange between solution and sediment phases. Hayes et al. (1952) calculated turnover times after adding ^{32}P-labeled phosphate to small lakes, assuming that exchange was a simple two-directional, first-order process. Turnover times of 5.4 to 40 days were estimated for dissolved inorganic phosphorus, and 30 to 176 days for phosphorus in solids, including sediments. Using a similar approach in laboratory experiments, Hayes and Phillips (1958) calculated turnover times ranging from 2 to 22 days for sediment inorganic phosphorus

in nonmixed systems. Results obtained after adding antibiotics to sediment-water systems were interpreted to show that sediment microorganisms were partially involved in the exchange process (Pomeroy et al., 1965).

The assessment of phosphorus exchange between sediments and waters is complicated by a number of factors, including the difficulty in obtaining accurate lake phosphorus budgets, redox reactions of iron components at the sediment-water interface, and the complexity of lake water circulation. Although a considerable amount of research on exchange has been done, the role of sediments in the uptake and release of sediment phosphorus, as influenced by sediment properties and environmental properties and environmental factors, is not fully understood (Syers et al., 1973).

Biochemical Availability

Hayes and Phillips (1958) used radiophosphorus and lake sediments to follow the phosphorus equilibrium relationships and rate of exchange between mud and water. They proposed that physiochemical and biological layering (undisturbed sample versus artificially mixed mud samples) of surface muds of lakes was unimportant to the exchange of phosphorus. They also pointed out that, both in the laboratory and in the field, the absence of oxygen in water overlying sediment would allow inorganic phosphorus to be released from the mud or sediment. They found the final level of total exchangeable phosphorus in waters is eventually determined by import of phosphorus by river inflow and the rate at which phosphorus is lost by incorporation into inorganic insoluable precipitates and undecayed organic matter. Therefore, detritus helps to determine the turnover rate for phosphorus in mud, bacteria, and plants; thus, in shallow waters the growth and bacterial decay of rooted aquatic plants dominates the phosphorus exchange. Also observed was a remarkable ability for bacteria to hold phosphorus in water; this might be accomplished in two ways: (1) by an acceleration of the rate ^{32}P was returned from the sediment to the water by bacteria in the mud; or (2) by the rapid uptake

of radiophosphorus by bacteria in the water and their ability to hold the radiophosphorus from the chemical or colloidal adsorption mechanism of the mud.

Release of sediment phosphorus to the overlying water occurs through suspension of particulate forms or transport of dissolved forms through turbulent mixing and diffusion. Release to the overlying water of dissolved inorganic phosphorus can occur if the concentration of interstitial dissolved inorganic phosphorus exceeds that in the overlying water (Stumm and Leckie, 1971). Keup et al. (1970) investigated the susceptibility of flood plain sediments to the release of nutrients. They found that the more organic phosphorus present in the soil, the greater the increase in leachate phosphorus concentration. They also observed that anaerobic water increased the rate of release of total phosphorus over that of aerobic water.

Odum et al. (1958) found it difficult to distinguish between biological assimilation and "physical uptake" because phosphorus in various forms is readily taken up through sorption by sediments and by organisms without being immediately incorporated into the protoplasm.

Pomeroy et al. (1965) suggested that sediments are a buffer (sorbing, storing, and gradually releasing) of phosphate content of the water and that the top ten centimeters of sediment contained sufficient phosphorus to replace that in water twenty-five times. He found that release of phosphorus from sediment could support a phytoplankton bloom, although only enough phosphorus was present in the water to support the photosynthetic rate for such a bloom for one day. Borchardt and Azad (1968) found that the critical phosphate concentration required for maximum algal growth decreased linearly with increasing temperature from $10^{\circ}C$ to $30^{\circ}C$. They hypothesized that this relationship may explain the sudden blooming of plankton after a warm spring day or after a warm rainfall.

The exchange of phosphorus between sediment and water combines the sorption reaction and the biologically controlled exchange, which

is probably between microorganisms and water. In a suspended sediment experiment on several Wisconsin lakes, Williams et al. (1970) found that sediments which adsorbed the most phosphorus during the first step (uptake step) usually released the least phosphorus during the subsequent desorption step regardless of how much phosphorus was added to suspended sediment samples.

Although several investigators (Williams, 1970; Armstrong et al., 1975; Fillos et al., 1972; and Fillos et al., 1975) arrived at phosphorus release and uptake rates, more detailed information is needed to establish sources and sinks of phosphorus and to establish the correct exchange rates between the various sources and sinks under actual or simulated natural environmental conditions.

Temperature And Salinity Effects On Nutrient Exchange

Marsh productivity and pathways of nutrients have been studied in detail by many investigators. However, studies concerning the investigation of the relationship between temperature, salinity, and nutrient exchange rates have been seriously neglected.

Temperature Effects On Exchange

Some mention of temperature effects on nutrient exchange has been included in the works of such investigators as Garritt and Goodgal (1954), Senstius (1958), Bremner et al. (1958), Keeney (1973), Muljadi et al. (1966), Foree et al. (1971), Lee (1970), and possibly others. From a review of these works, it may be seen that increased temperatures affect nutrient exchange rates by causing: (1) increased chemical reaction rates; (2) increased or decreased adsorption rates; (3) increased biological reaction rates; and (4) increased diffusion rates. Investigations which have established credence to some of the above temperature effects on nitrogen and phosphorus exchange rates are reviewed below.

It is generally concluded that higher temperatures favor decomposition over assimilation which influences regeneration, turnover, and assimilation of nitrogen. Foree et al. (1971) found that ammonification

proceeds at a measurable rate at low temperatures when assimilation is usually low. Nitrification rates in sediment-water systems have been shown by Chen et al. (1972a) to double with each $10^{\circ}C$ increase in temperature. Investigation by Bremner et al. (1958) has revealed the rate of denitrification in submerged soils was influenced by temperature with the optimum rate at $60-65^{\circ}C$ and slower rates at lower temperatures.

Higher temperatures favor sorption (uptake) of phosphorus, at least in suspension of sediment tests, as was pointed out by Carritt and Goodgal (1954). The extent of phosphorus adsorption was reported by Muljadi et al. (1966) to increase with temperature; however, adsorption is usually exothermic, leading to a decrease in adsorption with increased temperature.

Salinity Effects On Exchange

The only investigation which indicated conclusive results regarding salinity effects on nutrient exchange (using a slurry system) was reported by Carritt and Goodgal (1954). They found that removal of phosphorus was less in sea water than in fresh water although not in direct proportion to salinity. From this work and others along with text references on this subject, it appears that the increase in salinity affects nutrient exchange as follows: (1) decrease in diffusion rates, (2) decrease in sorption and desorption rates, (3) decrease of (or competition effect on) ion exchange sites of clay, and (4) increase or decrease in tolerance limit effects on biomass adaptation.

Summary

From the above it would appear there is a shortage of material in the literature on the temperature and salinity effects on nutrient exchange, and that additional work is needed in this area. Since little has been proven about the effects of temperature and salinity on rates or release from and uptake by sediments for nitrogen and phosphorus, the results obtained from this investigation and other recent experiments should provide a departure point from which more detailed study may determine exactly what mechanisms are affected by salinity and temperature in sediment-water nutrient exchange.

CHAPTER III
MATERIALS AND METHODS

INTRODUCTION

The experiments carried out in this study were confined to laboratory microcosm investigations and conducted at the Environmental Health Engineering Laboratory, The University of Texas at Austin, Austin, Texas. Continuous-flow reactors were operated using two modes of nutrient exchange, leaching and uptake, to determine exchange rates between sediment-water systems. Replicate microcosm reactors were exposed to three different temperature and salinity conditions each for a total of nine temperature-salinity combinations.

MATERIALS

Source of Sediment Cores

The Texas·Gulf coast has many estuaries which are fairly extensive in area, shallow, and generally well-mixed. Many have islands and marshy areas along the land-water boundary. The previously selected study area (Armstrong et al., 1975) adjacent to Swan Lake is a low, wet marsh on a two-mile peninsula situated between the Lavaca River and Swan Lake (see Figure III-1).

Samples were collected from the study area on 12 March 1975. The weather at the time was fair and warm with a daytime high temperature of $75^{\circ}F$. The marsh was relatively dry with no evidence of recent flooding. Water levels were such that most of the marsh grasses were periodically inundated.

A total of 14 sediment core samples were removed from an area (5 by 10 meters) of quiet water with a depth of 30 to 50 centimeters. This area was adjacent to an established flow channel leading to a tributary that in turn feeds Swan Lake (see Figure III-1).

FIGURE III-1

LOCATION OF FIXED-BED SAMPLE SITE

Scale: 1 inch – 2000 feet

SWAN LAKE

Core and Reactor Sites → X

Field Stations →

LAVACA RIVER

LAVACA BAY

Sewage Disposal

Windmill

CATFISH BAYOU

1593
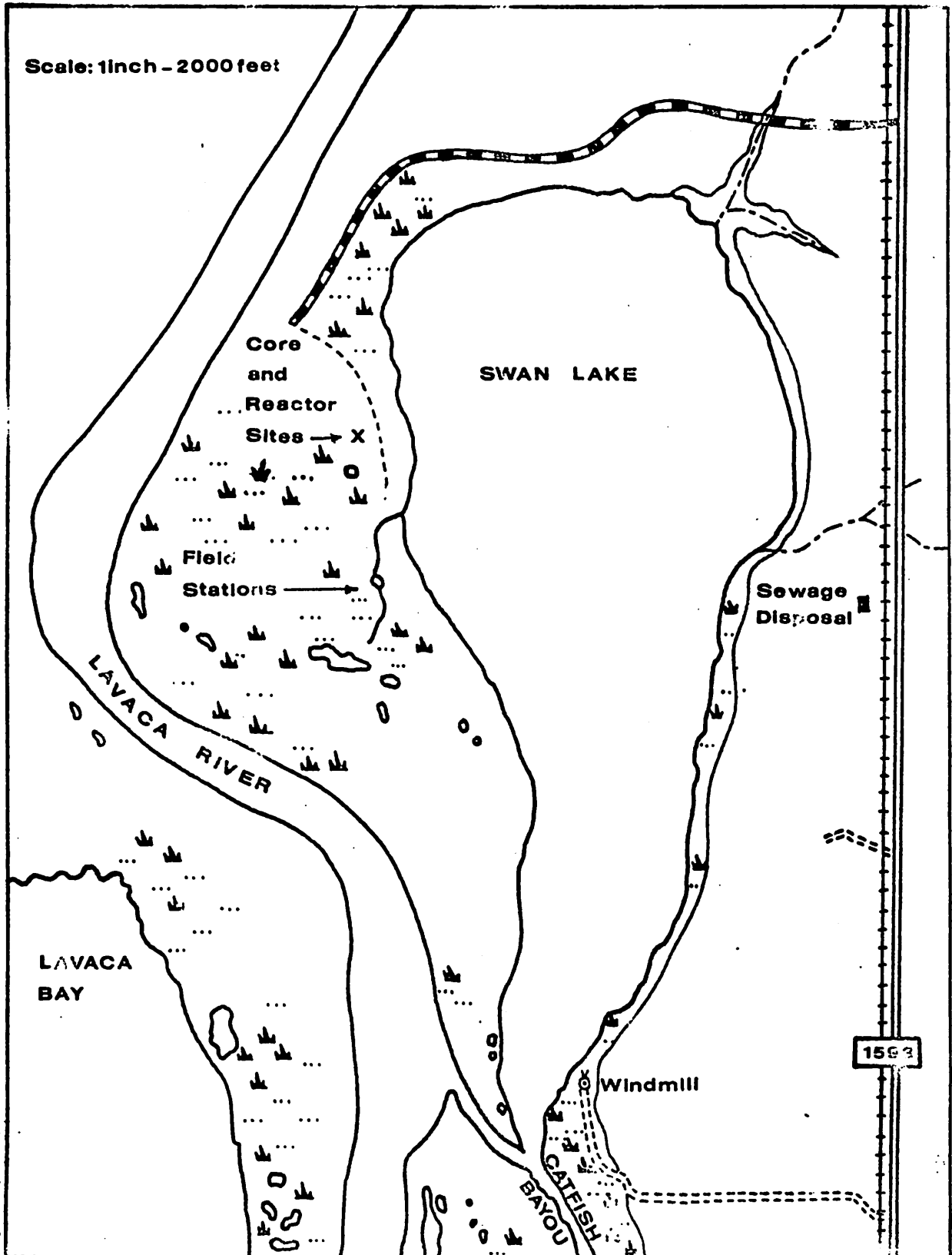
Slightly turbid, brackish water was noted at the site. The pH of the water overlying the core samples taken on arrival at the laboratory ranged from 7.6 to 8.0. Analysis of a composite sample of this same water gave the following results: ammonia-N = 1.7 mg/l; nitrate-N = 0.08 mg/l; nitrite-N = 0.04 mg/l; and orthophosphate-P = 0.72mg/l.

Microcosm Design

Establishment of Microcosms

Sediment was removed from the field site by pushing six 40-cm long cylindrical (13.8 cm diameter) sections of plexiglas and eight 50-cm long PVC pipe (10.2 cm diameter) sections into the bottom sediment in shallow water, avoiding emergent grasses and algal mat areas, then carefully lifting and stoppering the cylinders with rubber sheeting at the bottom. Although the cores were taken from a relatively small area, there were noticeable differences in soil consistency, especially the loosely-mixed top layer of sediment. Depths of sediment averaged 12 cm in the plexiglas reactors and 16 cm in the PVC reactors. These fixed-bed reactors were brought to the laboratory, and existing water was maintained over the sediment until laboratory experiments were started. Additional estuarine water collected at the site was used to maintain selected levels until all leaks were stopped and to replace evaporated water. To prevent anaerobic conditions, air was bubbled through the water of all reactors periodically.

All 12 reactors were placed in an air conditioned laboratory and maintained at $23^{\circ}C$ to $26^{\circ}C$ until two days prior to the beginning of the leaching experiment. At that time three PVC reactors (Reactors 1, 2, and 3) were placed in a $4^{\circ}C$ constant temperature room and three PVC reactors (Reactors 4,5, and 6) were placed in a $15^{\circ}C$ constant temperature room. Three salinity levels were used in these tests, 0, 10, and 20 ppt; reactor sets 1 and 4, 2 and 5, 3 and 6 were maintained at these three salinity levels, respectively. The plexiglas reactors (Reactors 7 through 12) remained in the $23^{\circ}C$ to $26^{\circ}C$ laboratory throughout the first series of the leaching experiments. Reactor sets 7 and 8, 9 and

10, and 11 and 12 were kept at salinities of 20, 10, and 0 ppt, respectively. After the leaching experiments, all reactors were placed in the 4°C room for storage until the start of the uptake experiments three weeks later.

Equipment

Reactors: The reactors contained ample amounts of sediment to interact with the overlying waters. The larger diameter plexiglas reactors were provided with 2 liters of overlying water, while the smaller diameter PVC reactors were provided 1 liter. Water depths were 13.3 cm in the plexiglas and 12.33 cm in the PVC reactors. The areas of the two sediment surfaces were 150.4 cm^2 and 81.07 cm^2 respectively for the two sizes of reactors and thus the sediment surface area to water volume ratios were approximately the same for both size reactors.

Other Components: Flow-through systems were established with a detention time of 12 hours in all reactors. Cole-Parmer Instrument Company pumps were used to maintain rates of flow of four liters per day for the plexiglas reactors and two liters per day for the PVC reactors. Flow rates were checked and adjusted if necessary at each sampling time. Drip feed lines were run to the reactors from the pumps and a constant-level siphon was installed in each reactor to maintain established water volumes in the reactors.

Five-gallon (18.93 liter) glass carboys were used for influent water storage and had level gauges on the side used to monitor rates of removal of water. As a water quality control measure, the large reactor feed bottles were connected three in series. Water drawn from these feed bottles was split into two lines for pumping to the two reactors with identical salinity (see below). In addition, another series of containers was used to collect each reactor's effluent for exact flow measurement.

Adequate stirring was maintained for the six plexiglas reactors by a bank of jar stirrers turning at approximately 15 rpm. Individual, slow-mixing stirrers with rheostat speed controls were installed on each of the PVC reactors.

Physical Controls

Temperatures remained constant within two degrees for the $4^{\circ}C$ and $15^{\circ}C$ reactors, while the temperature in the air conditioned laboratory fluctuated between $23^{\circ}C$ and $26^{\circ}C$. The six plexiglas reactors were kept in a well-lighted laboratory with western window exposure to daylight. The six PVC reactors were kept in dark conditions throughout the experiments and all reactors were maintained in the $4^{\circ}C$ dark room for the three weeks between the leaching and uptake experiments. This was done to discourage algal and bacterial growth between experiments.

Assembly

Figure III-2 illustrates the overall layout of the two reactor systems. The six plexiglas reactors (Reactors 7 through 12) are pictured in the top photograph while the PVC reactors (Reactors 1 through 3 and another identical system with Reactors 4 through 6) is shown in the bottom photograph.

Description of Operation

The objective of providing a constantly-stirred, flow-through reactor system for each water-sediment microcosm was met by the physical setup described. The initial leaching experiment was conducted for five days, followed by a three-week equalization interval and then a second five-day uptake experiment. Since all sediment samples were removed from the field site without visible algal mat or plant growth, photosynthetic activity in the laboratory was not desired. Light regimes, therefore, were not imposed on the systems, although some light effects were present in the laboratory. In a later, thirty-day experiment, a light regime was imposed on the six plexiglas reactors. Results of that experiment indicated strong responses by bacterial and algal communities in the microcosms to the varied salinities. Large growths of algae and bacteria occurred at 10 ppt salinity, followed closely by growth in the 20 ppt salinity reactor. Little algal and bacterial productivity was apparent in the reactors with 0 ppt salinity through the first 15 days, but a more noticeable growth occurred by the end of 30 days.

As estuarine water from the field was present initially in all reactors, the beginning step was to drain and replace this water with the test influent waters which contained 0 ppt, 10 ppt, and 20 ppt salinity. Because the tap water contained varying amounts of ammonia which persisted in the distilled water, water that had been distilled and deionized was used to make up simulated brackish water of 10 ppt and 20 ppt salinities using *INSTANT OCEAN* salts. Some variation in the phosphorus and nitrogen levels was noted in different batches of this simulated brackish water during leaching experiments. Later, the uptake experiments were provided simulated brackish water that had been pooled before being aliquoted into bottles for storage and use. Nutrients were added to the influent waters during the uptake experiments to achieve final concentrations of 5 mg/l ammonia-N and 2 mg/l of ortho-phosphate-P.

Sampling Procedures

Schedule

The frequency of sampling was controlled by two factors: (1) the large sample volumes required for analyses (400 ml each or 40 percent of the volume of the small reactors); and (2) the anticipated initial rapid rates of leaching and uptake for the first one to two days and the frequent sampling needed to detect and measure these rates. These demands were conflicting, so a compromise schedule and procedure was developed in which samples were taken at 3, 6, 12, 24, 36, and 48 yours followed by daily sampling up to five days for both leaching and uptake modes. To compensate for the large volume removed initially, the small reactors were filled with makeup water after the first 3-hour sampling.

In order to determine the concentration of nutrients in the influent water, samples were taken at 0, 2.5 and 5 days after the start of the experiments.

* Aquarium Systems, Incorporated, Eastlake, Ohio.

Other Samples

Samples of sediments from the two spare reactors were removed, dried and sent to the Texas A&M University Soils Testing Laboratory for detailed soil analysis. After completion of the uptake experiments, another sample was made up from the top 10 centimeters of Reactor 4 for use in a simple, suspended-sediment leaching experiment which lasted for six days. Results of these tests are given in Chapter IV.

Laboratory Tests

The sampling schedule described above was designed to give nitrogen and phosphorus concentrations from all the reactors at their various temperatures and salinities and under different modes of operation. Chemical analyses were performed by the Texas State Department of Human Resources Laboratory.

Samples were initially checked for pH in the laboratory using a Beckman Zeromatic pH meter. For the leaching experiments, samples were preserved with 2 mg/l of sulfuric acid and stored at $4^{\circ}C$ until taken to the Laboratory where they were analyzed usually on the same day received. For the uptake experiments, samples were not chemically preserved but merely stored at $4^{\circ}C$ until analyzed (again on the same day delivered) in an attempt to improve analysis accuracy.

Physical variables monitored during the experiment were: sample water temperature, ambient air temperature, flow rate, and dissolved oxygen concentrations in reactors. At times, visual observations were made of reactors as well as equipment, and records were kept of equipment malfunctions. Dissolved oxygen was monitored utilizing a Precision Scientific Company galvanic cell oxygen analyzer. Temperature and salinity corrections were applied to observed dissolved oxygen levels based on nomograph tables provided by the manufacturer, and conductivity measurements were used to determine effluent salinity levels.

METHODS USED

Experimental Rationale

Basically no new methods were used in these experiments that have not been reported by others; however, the use of flow-through water-sediment microcosms to obtain nutrient exchange rates and the effects of temperature and salinity on those rates had not been applied in exactly the same way as used in these studies. The imposition of controls on influent nutrient concentrations and flow rates was felt to be requisite to achieving accurate results.

To calculate the nutrient release and uptake rates from the sediments, a materials balance was computed for each reactor. For example, the nitrogen release rate in $mg/m^2/day$ was calculated using the mass balance model represented by the following equation

$$\frac{dS}{dt} = \frac{Q}{V}(S_o - S) - f(\text{sediment}) - f(\text{algae and bacteria}) \qquad \text{(III-1)}$$

where

$\frac{dS}{dt}$	=	the change in nutrient concentration in the reactor with time (mg/l/day)
$\frac{Q}{V}(S_o - S)$	=	concentration change due to influent gains and effluent losses
f (sediment)	=	nutrient concentration changes due to exchange with sediments
f (algae and bacteria)	=	nutrient concentration changes due to exchange with algae and bacteria communities
Q	=	flow-through rate (liters/day)
V	=	reactor water volume (liters)
S_o	=	influent nutrient concentration (mg/l)
S	=	effluent nutrient concentration (mg/l).

For steady-state conditions

$$\frac{dS}{dt} = 0$$

and

$$\frac{Q}{V} (S_o - S) = f \text{ (sediment, algae and bacteria)}. \qquad \text{(III-2)}$$

Equation III-2 will also hold when dS/dt approaches zero even though non-steady state conditions prevail. Assuming that dS/dt is small compared to Q/V ($S_o - S$) but that dS/dt $\neq 0$, Equation III-1 may be modified to Equation III-2 and integrated numerically (using the technique of a modified trapezoidal rule for approximating the area between an arc of the nutrient concentration curve and the base, or zero, concentration) to obtain the nutrient exchange rates due to sediments and algae and bacteria combined. Using the modified trapezoidal rule, a numerical solution to obtain the mass exchanged between the sediment-algae-bacteria system and the overlying water was approximated by the general equation

$$\text{Mass of nutrient exchanged} = \text{Average concentration} \times \text{Flow} \times \text{time} \times \frac{1}{\text{area}}$$

or

$$L = \left(\frac{C_{t_1} + C_{t_2}}{2}\right) QT\frac{1}{A} \qquad \text{III-3}$$

where

L   =   Mass exchanged from time t_1 to t_2 with the sediment surface area $(mg/m^2/day)$,

C   =   observed concentration at time t_1 or t_2 corrected for influent concentration (mg/l),

Q   =   flow rate through reactor (l/d),

A   =   sediment surface area in reactor (m^2),

T   =   time between nutrient sampling periods $(t_2 - t_1)$ (days).

CHAPTER IV

RESULTS

INTRODUCTION

The data obtained from the nutrient uptake and release experiments described in Chapter III were carried through mass exchange calculations to determine nutrient exchange rates. These concentration and mass exchange data are presented in this chapter in sections on temperature and salinity effects on release and uptake modes.

BOUNDARY CONDITIONS FOR REACTORS

Influent Water

Control of influent water quality was a major problem. Influent water, although stored in glass bottles, often showed a slight ammonia loss (in both spiked and unspiked waters). The average loss for all reactor feed systems for the uptake experiment was 0.04 mg/l of nitrogen over a five-day period. High concentrations of nitrogen and phosphorus were found in influent water in which low background concentrations were desired. These occurred in the brackish water mixtures of INSTANT OCEAN and caused uptake to take place during the leaching experiment. Other changes were apparent when concentration levels in ammonia-spiked waters either changed or laboratory errors indicated that effect. The nutrient background changes in turn required some correction. For the leaching experiments, background levels of nitrogen and phophorus were present in proportion to the concentration of INSTANT OCEAN used. The backgound ammonia-N concentrations for 20, 10, and 0 ppt salinities were 0.011 mg/l, 0.006 mg/l and none, respectively.

Sediment Characteristics

Two sediment microcosms were not utilized in the experiments and were dismantled, quartered, and used for soil analysis. The soil

analyses were made by The Agricultural Extension Service Soil Testing
Laboratory at Texas A&M University. The results are given in Table
IV-1.

Reactor pH and Dissolved Oxygen

Dissolved oxygen concentration and pH of the water samples from
the reactors were determined at the scheduled sampling times during
the two laboratory experiments. The results of the analyses are sum-
marized in Table IV-2 (leaching phase) and Table IV-3 (uptake phase).
Results for Table IV-2 show aerobic conditions (4.3-12 mg/l of dis-
solved oxygen) throughout the experiment and overall pH ranges of 7.1
to 8.6. The uptake phase results (Table IV-3) show a range of 4.5-
11.5 mg/l of dissolved oxygen and pH ranges of 6.1 to 8.2.

NUTRIENT EXCHANGE CONCENTRATIONS

The following presentation of results of the exchange experiments
includes a representative number of example graphs of concentration
levels versus time since the more meaningful results are those con-
cerning mass of nutrients exchanged.

Nitrogen

Figure IV-1 presents results of exchanged nitrogen concentration
levels, (S_o-S), for selected representative reactors during the leaching
mode of the experiment. The reactor effluent nitrogen concentration, S,
has been subtracted from the influent nitrogen concentration, S_o, to
obtain these results. Results for the three temperature and salinity
conditions are shown in these graphs. The four reactors (Reactors 3,
6, and 11 and 12) with 0 ppt salinity were lacking in buffering, at least
initially, until leaching from the sediment cores gradually increased
both the buffering and the pH values. Changes in concentrations of
nitrogen and phosphorus shown in the next four figures (Figures IV-1
through IV-4) are attributed to increase (leaching) or depletion (uptake)
of nutrients in flow through waters. Results were obtained from anal-
yses of frequent sampling over the five days of the two experiments and

TABLE IV-1

CORE SAMPLE SOIL NUTRIENT ANALYSIS

Analysis	Sample	
	1	2
pH	7.1	7.0
Magnesium (ppm)	> 250	> 250
Potassium (ppm)	600	600
Organic Material (%)	4.2	4.0
Iron (ppm)	> 20	> 20
Copper (ppm)	1.66	1.66
Calcium (ppm)	>3000	>3000
Phosphorus (ppm)	46	21
Sodium (ppm)	>1250	>1250
Zinc (ppm)	2	2
Manganese (ppm)	> 10	> 10

TABLE IV-2

WATER QUALITY IN SEDIMENT REACTORS DURING LEACHING PHASE

Reactor No.	Salinity (ppt)	Temperature (°C)	Dissolved Oxygen Range (mg/l)	pH Range
1	20	4	8.3-10 3	8.15-8.7
2	10	4	7.2-10.6	7.3-8.7
3	0	4	7.7-12.0	7.1-8.0
4	20	15	5.1- 5.9	7.7-8.2
5	10	15	5.4- 6.9	7.6-8.4
6	0	15	6.7- 7.7	7.6-8.2
7	20	23	4.3- 6.4	7.9-8.3
8	20	23	4.5- 6.4	8.1-8.5
9	10	23	4.7- 6.0	7.5-8.5
10	10	23	4.8- 6.8	7.6-8.5
11	0	23	5.8- 6.8	7.2-8.6
12	0	23	5.7- 6.7	7.3-8.1

TABLE IV-3

WATER QUALITY IN SEDIMENT REACTORS DURING UPTAKE PHASE

Reactor No.	Salinity (ppt)	Temperature (°C)	Dissolved Oxygen Range (mg/l)	Range pH
1	20	4	7.4-10	7.9-8.2
2	10	4	8.0-10.7	7.2-7.5
3	0	4	8.4-11.5	6.1-7.1
4	20	15	5.8- 8.1	7.8-8.0
5	10	15	6.2- 8.8	7.2-7.5
6	0	15	6.1-10.3	6.1-6.9
7	20	23	4.8- 6.0	7.3-7.9
8	20	23	4.8- 6.4	7.4-7.8
9	10	23	5.2- 6.8	7.0-7.4
10	10	23	4.5- 6.8	6.8-7.4
11	0	23	5.8- 7.2	5.9-6.8
12	0	23	5.5- 7.2	5.8-6.6

FIGURE IV-1
RELEASE OF NITROGEN BY MARSH SEDIMENTS

Reactor 3. 0 ppt Salinity at 4°C

• – Ammonia
o – Nitrate
▪ – Nitrite
♦ – Total (NH₄, NO₃ & NO₂)

(a)

Reactor 5. 10 ppt Salinity at 15°C

(b)

Reactor 7. 20 ppt Salinity at 23°C

TIME (days)

(c)

IV-6
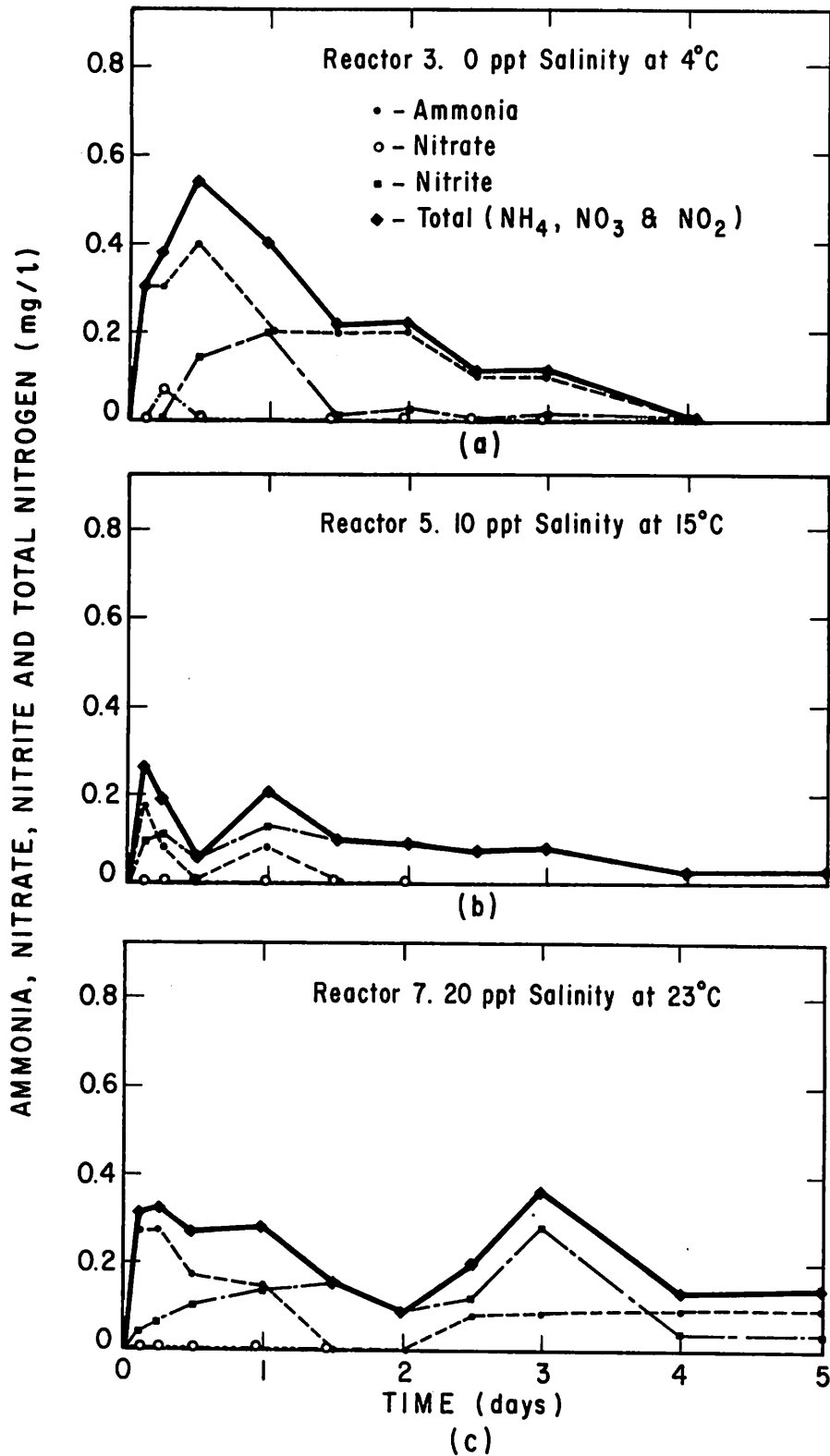
FIGURE IV-2
UPTAKE OF NITROGEN BY MARSH SEDIMENTS
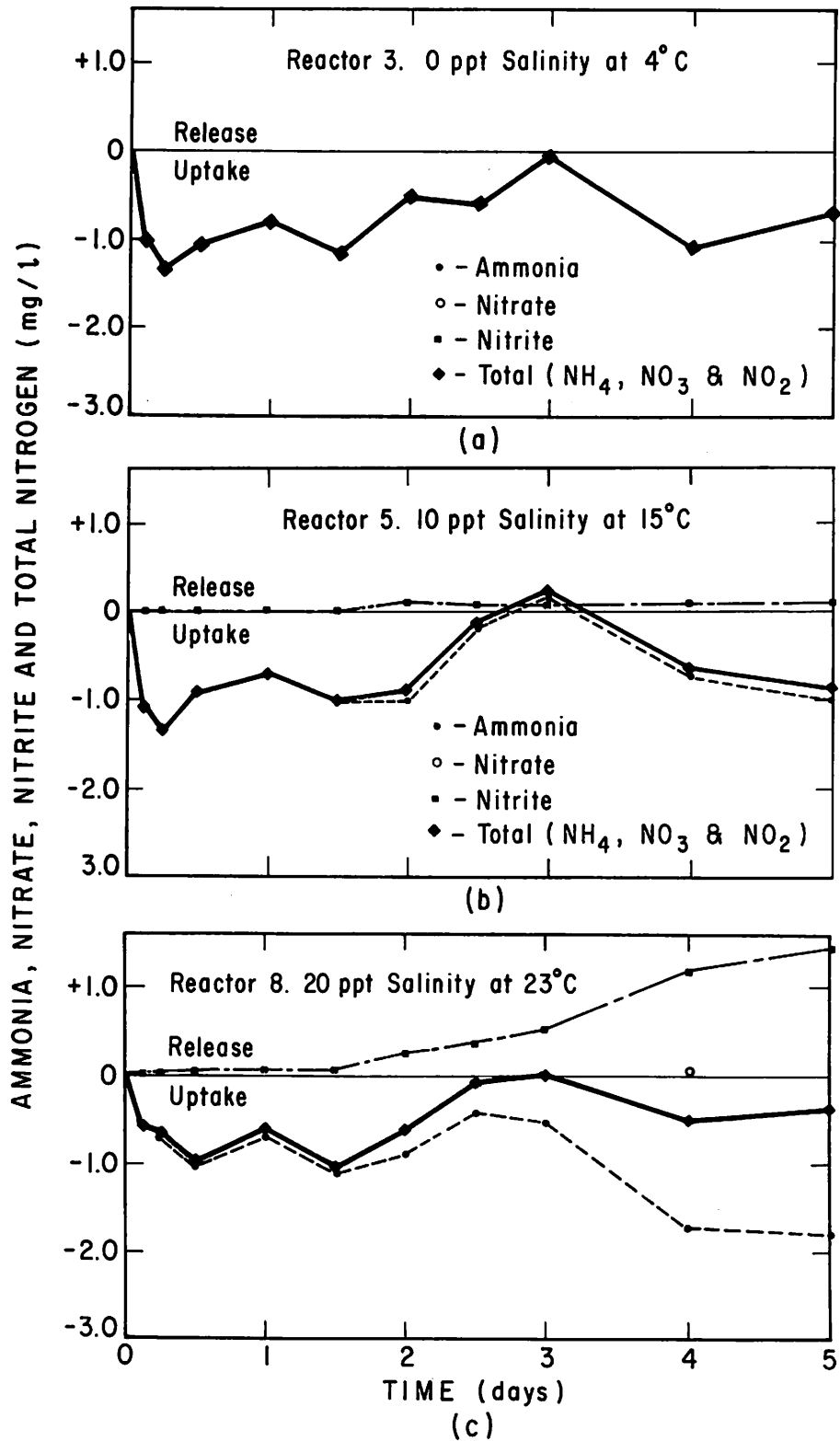
FIGURE IV-3
RELEASE OF PHOSPHORUS BY MARSH SEDIMENTS

ORTHOPHOSPHATE AS $PO_4 - P$ (mg/l)

Reactor 3. 0 ppt Salinity at 4°C

(a)

Reactor 5. 10 ppt Salinity at 15°C

(b)

Reactor 7. 20 ppt Salinity at 23°C

TIME (days)

(c)

FIGURE IV-4
UPTAKE OF PHOSPHORUS BY MARSH SEDIMENTS
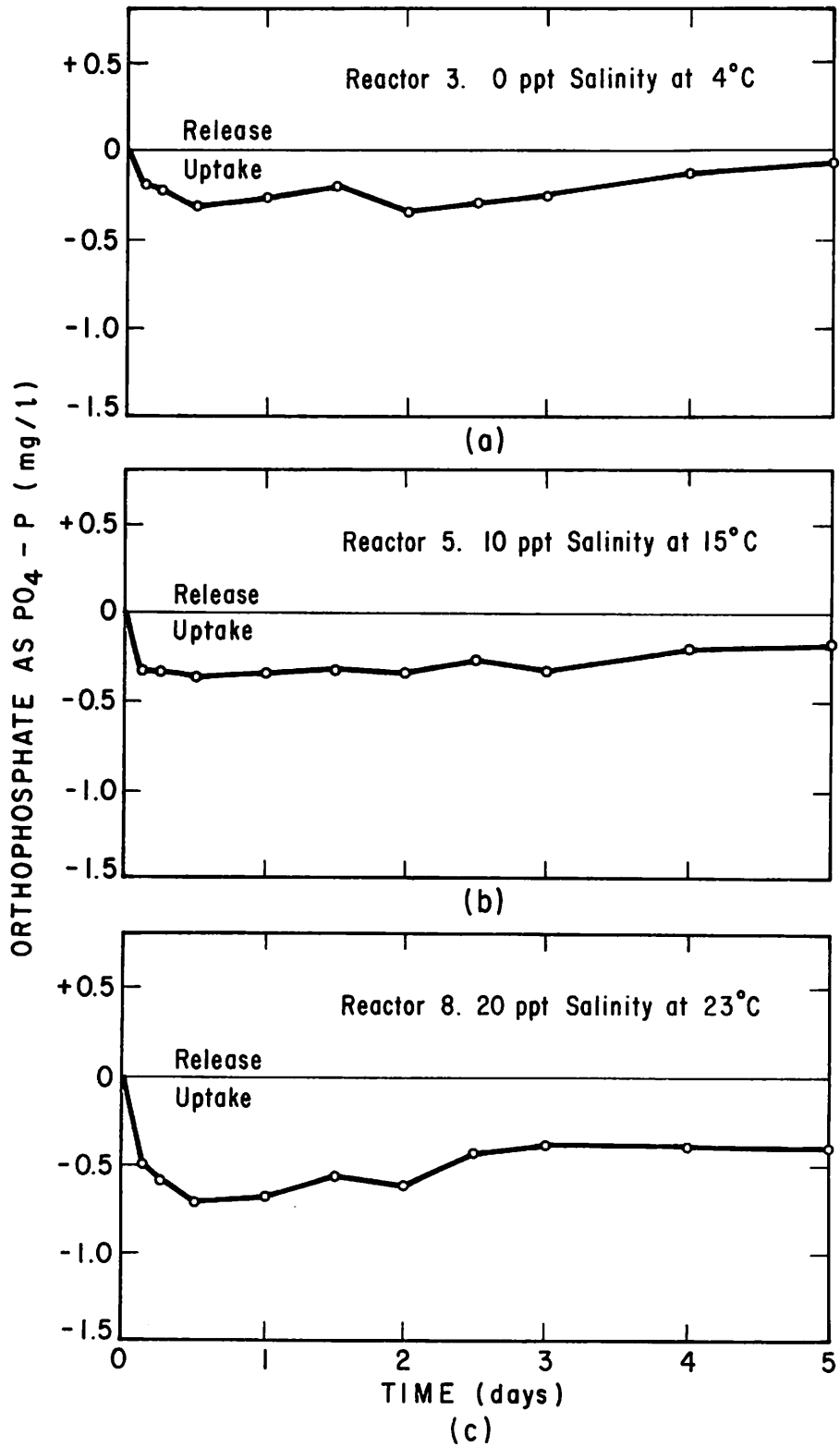
are not directly due to temperature or salinity conditions of the various reactors. Leaching rates were affected slightly in Reactors 7 through 12 when a stirrer malfunctioned and was replaced by another which would not function at low speed settings. This caused sediment scour and increased leaching concentrations for nitrogen and phosphorus from day two through five. The increased stirring at two days will be noted as a second peak in the leaching curves for Reactor 7 (Figure IV-1c). Reactors generally reached equilibrium or zero leaching levels by the end of the fourth or fifth day.

The three graphs in Figure IV-2 are examples of observed nitrogen uptake concentrations which have been corrected for influent levels of ammonia-N. It is apparent that nitrification is occurring, especially in Reactor 8 (Figure IV-2c). Nitrification was greatest at the higher temperatures and salinities and did not occur in 0 ppt salinity reactors at $4^{O}C$ and $15^{O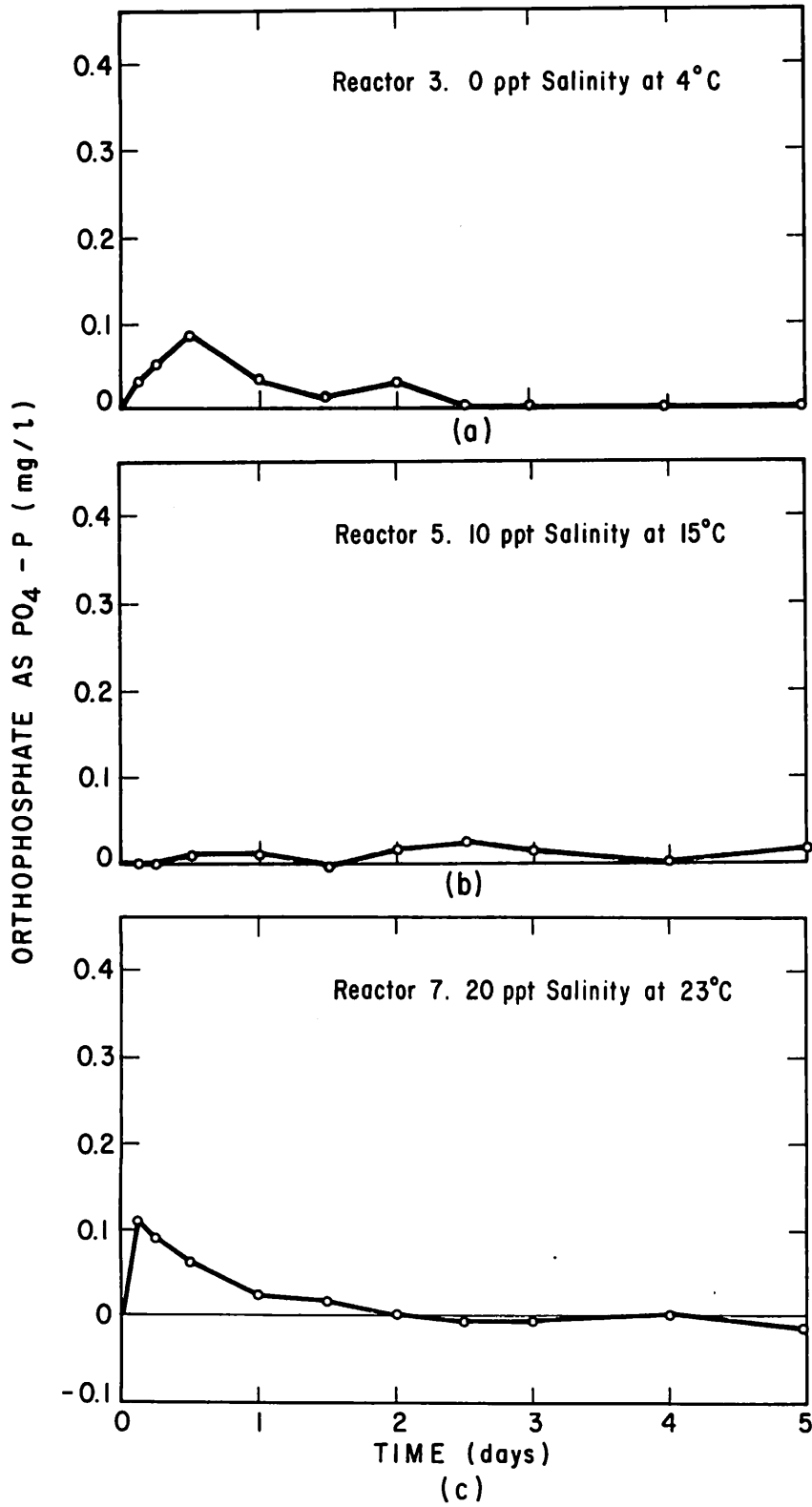}C$. A small concentration of nitrites did build up in the two 20 ppt, $23^{O}C$ reactors. Uptake reactions generally did not reach equilibrium and only passed through zero uptake as a transient condition. Most reactors reached a transitory zero uptake level at 2 to 2.5 days, but the 0 ppt salinity reactors were less consistent in approaching zero.

Phosphorus

Example graphs of the phosphorus exchanged in the leaching experiments are shown in Figure IV-3. Because dissolved inorganic phosphorus is the "available" form of phosphorus for aquatic plants and frequently constitutes the major portion of the total phosphorus in sediments, orthophosphate was the form examined with a view to understanding the role of sediments in removing dissolved phosphorus from, and releasing dissolved phosphorus to, overlying waters. Again effluent concentrations were subtracted from influent concentrations to obtain the exchanged concentrations. Generally, equilibrium conditions for phosphorus leaching were reached in four or five days, but some microcosms. released for longer times, particularly two of the six large reactors (Reactors 11 and 12 with 0 ppt salinity) which was probably due to increased stirring action at the two-day time. Most phosphorus leaching was completed by 2 to 2.5 days.

Figure IV-4 contains results of phosphorus uptake concentrations with time. A fairly steady uptake reaction is apparent through five-days. Only two reactors indicated conditions approaching zero uptake. Some reactors showed higher uptake concentrations for about 1.5 days, then reduced somewhat and leveled off for the remainder of the five days.

CUMULATIVE NUTRIENT EXCHANGE

Mass Balance Model

In order to arrive at nutrient release and uptake rates, results from the reactors were used in the nutrient mass balance model discussed in Chapter III. After the influent concentrations were subtracted from the reactor concentrations according to Equation III-3, the mass exchange of each nutrient was calculated. These mass exchange rates were in turn cumulatively added (integrated) and graphed. Example graphs of the cumulative mass of nutrients released are shown in Figure IV-5 and taken up in Figure IV-6. The curves will exhibit a negative slope or loss of mass if uptake occurs during the release mode or if release occurs during the uptake mode.

These results were used further to calculate the daily mean nutrient mass leached and taken up for each successive day, and they were then applied as data points or ranges to construct the graphs of temperature and salinity effects on nutrient concentrations which will be shown later in this chapter.

Temperature Effects

In order to compare the effects of temperature on the rates of nutrient exchange between the sediment and water, two analyses were performed. First, the nutrient exchange data were compiled for each reactor and each day of the experiment, the daily mean and range calculated and grouped according to the temperature at which the reactors were operated, and these mean values and ranges graphed versus time. Second, the nutrient cumulative mass data were compiled and graphed. Third, the mass exchange rates were calculated for successive days in the experiment and tabulated.

FIGURE IV - 5a
CUMULATIVE LEACHED NITROGEN
FROM MARSH SEDIMENTS

Reactor 3, 0 ppt Salinity at 4°C
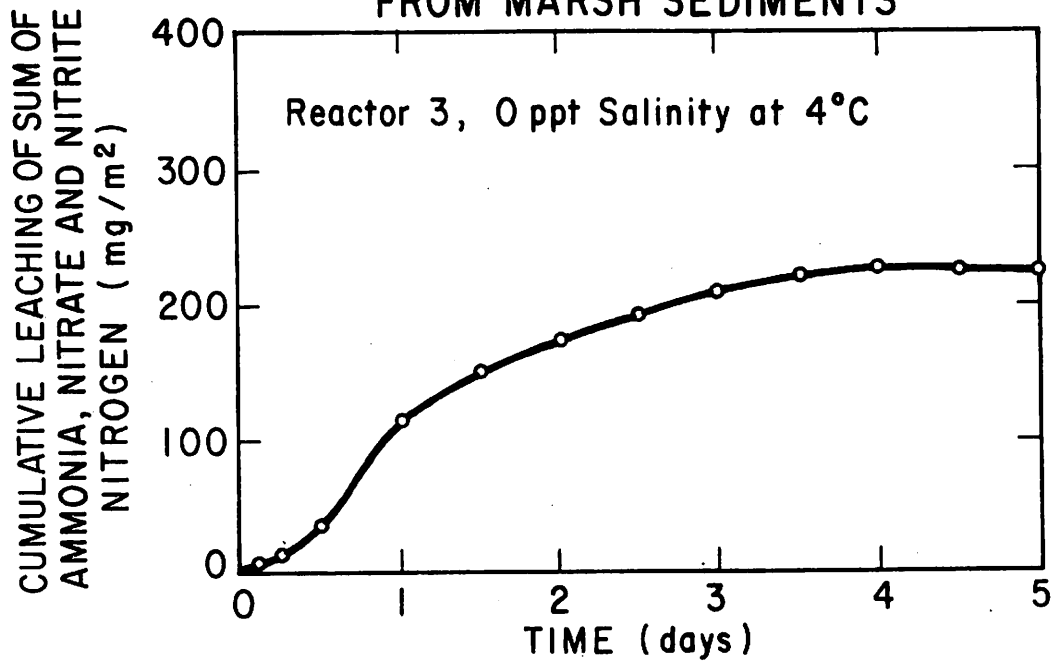
FIGURE IV - 5b
CUMULATIVE LEACHED PHOSPHORUS
FROM MARSH SEDIMENTS

Reactor 3, 0 ppt Salinity at 4°C
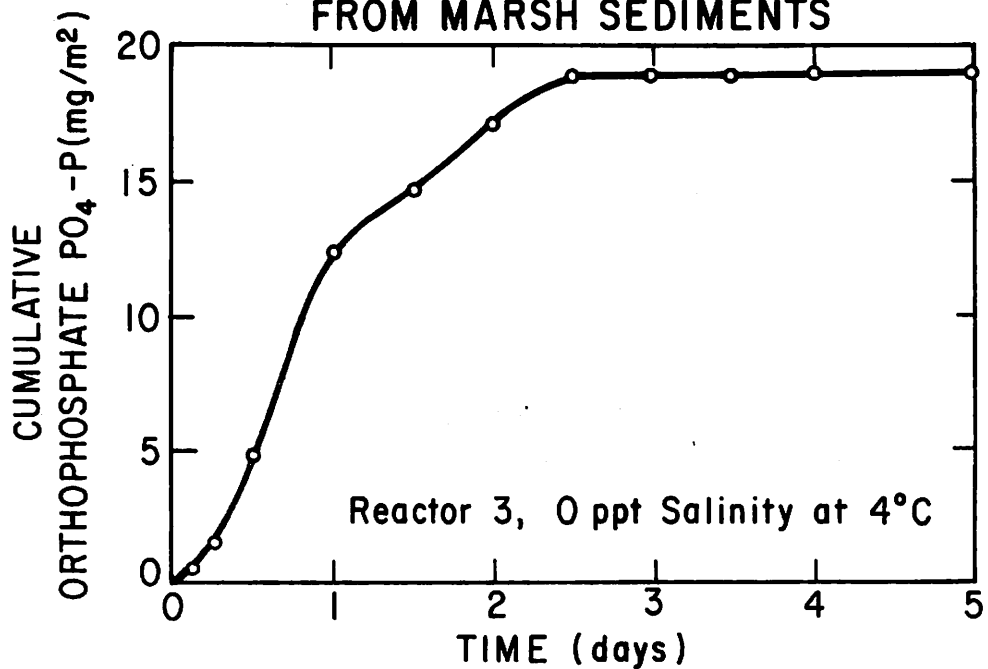
FIGURE IV – 6a
CUMULATIVE UPTAKE OF NITROGEN
BY MARSH SEDIMENTS

Reactor 8, 20 ppt Salinity at 23°C

CUMULATIVE UPTAKE OF SUM OF AMMONIA, NITRATE AND NITRITE NITROGEN (mg/m²)

TIME (days)
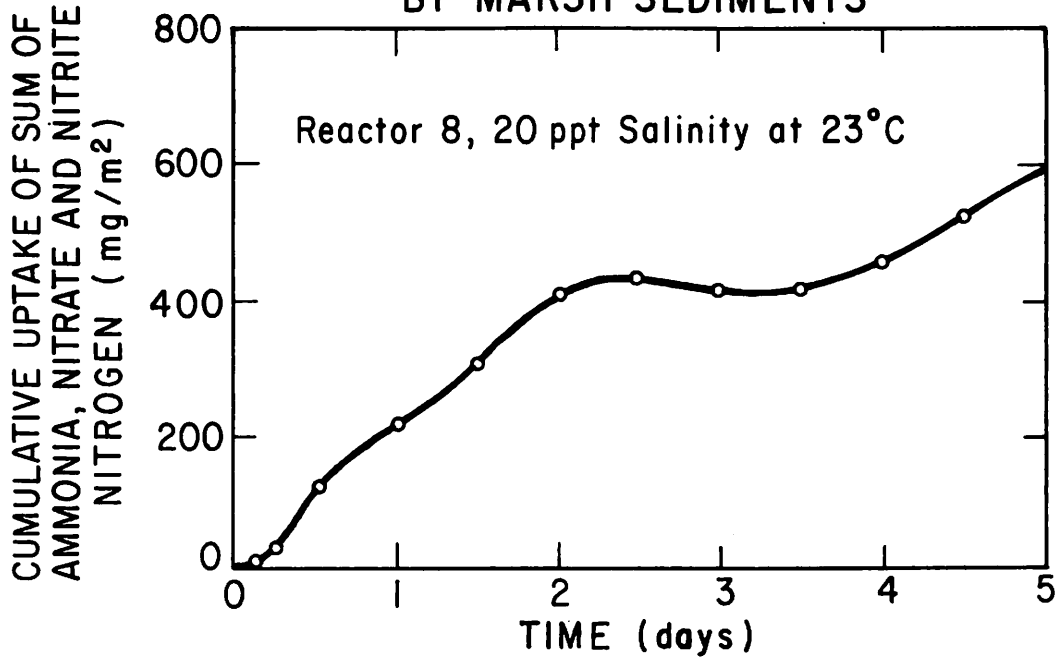
FIGURE IV – 6b
CUMULATIVE UPTAKE OF PHOSPHORUS
BY MARSH SEDIMENTS

Reactor 8, 20 ppt Salinity at 23°C

CUMULATIVE UPTAKE OF ORTHOPHOSPHATE PO_4 -P(mg/m²)

TIME (days)

IV-13
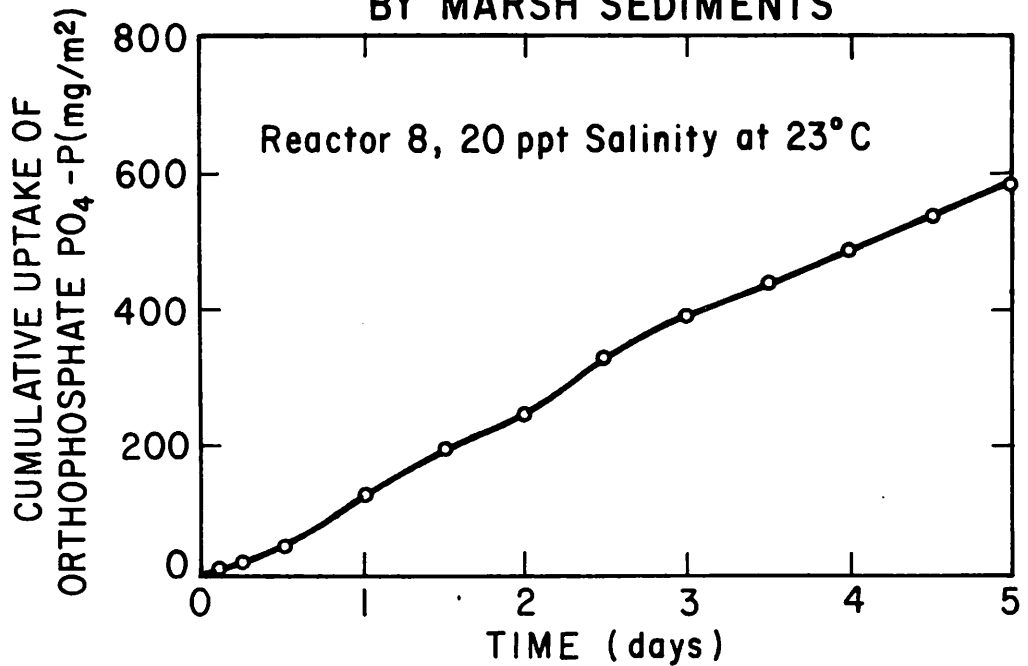
The same procedure was used to compile data for an examination of salinity effects.

Nitrogen

Results of temperature effects on the release of nitrogen are presented in Figure IV-7 and Table IV-4. Little temperature effect on nitrogen leaching rates is apparent at $4^\circ C$ and $15^\circ C$. The higher nitrogen concentrations and cumulative mass at $23^\circ C$ may reflect increased biomass productivity at higher temperature resulting in more ammonia produced from mineralization and ammonification as noted earlier in Keeney (1973). The $15^\circ C$ curve which should fit in mid-range, does not follow this rationale; its displacement could be caused either by less organic substance available for ammonification and mineralization or by a tighter clay sediment which could result in a net release less than the $4^\circ C$ reactors.

The temperature effects on nitrogen taken up by the sediments are shown in Figure IV-8 and Table IV-5. The curves for all reactors started at nearly equal concentrations and are nearly parallel until the third day. The $4^\circ C$ reactors reached equilibrium (mean of concentrations) at three days and stayed at that level for one day, then approached the $23^\circ C$ reactors uptake curve at five days. The highest concentration levels were maintained by the $14^\circ C$ reactors and are ascribed to less availability of organic materials. The depletion of organic material provides less ammonia through ammonification and mineralization resulting in a depleted nitrogen pool which in turn places a continued demand on the spiked waters throughout the five days. The slightly higher nitrogen concentrations in the $23^\circ C$ reactors over the $4^\circ C$ reactors at the third and fourth days is probably due to differences in biomass production and net effects from increased ammonia utilization at the higher temperature. The effects of temperature on mass of nitrogen taken up by the sediments follows the trends shown by the concentration curves.

FIGURE IV-7
TEMPERATURE EFFECTS ON NITROGEN
LEACHED FROM SEDIMENTS
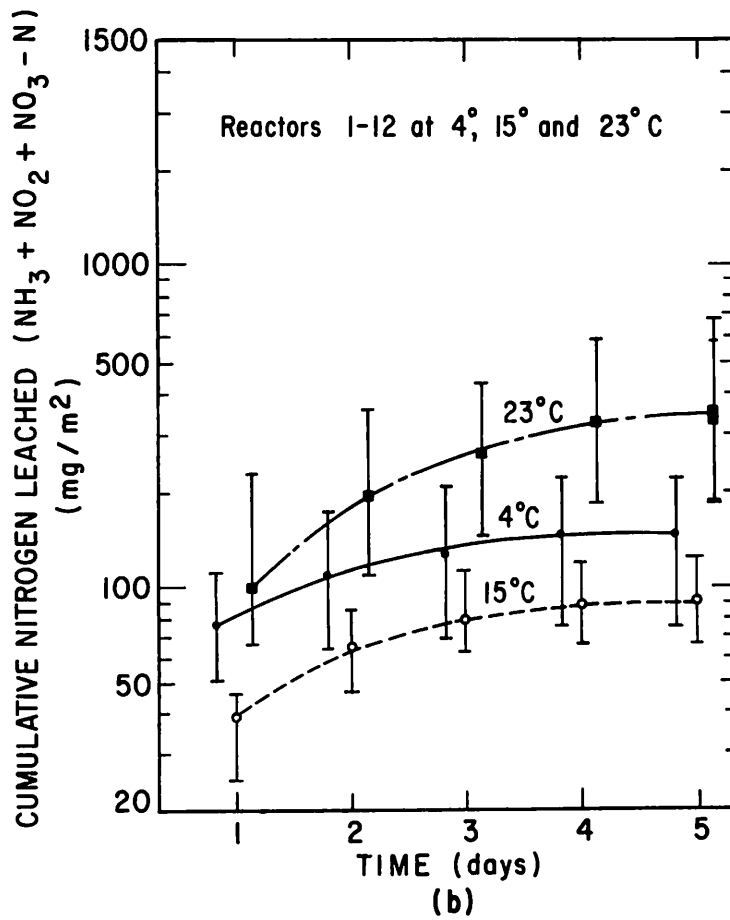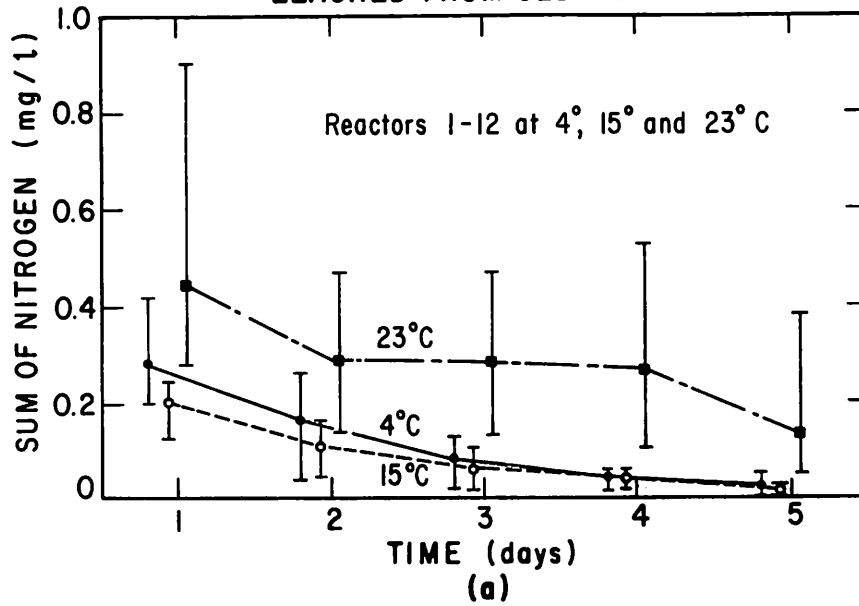
TABLE IV-4

TEMPERATURE EFFECTS ON LEACHING RATES
OF NITROGEN FROM SEDIMENTS

| Reactor Temperature (°C) | Time (days) | Nitrogen[1] Leaching Rates | | |
		Range (mg/m²/d)	Average (mg/m²/d)	Daily Average (mg/m²/d)
4	1	51-114	75	
	2	34-87	58	
	3	23-69	45	
	4	19-56	37	
	5	15-45	30	
15	1	25-46	39	
	2	24-42	32	
	3	21-36	26	
	4	17-31	22	
	5	13-25	18	
23	1	68-227	113	
	2	54-175	94	
	3	51-153	85	
	4	45-148	81	
	5	38-138	74	
All Temperatures	1			75
	2			61
	3			52
	4			47
	5			41

[1]Nitrogen = $NH_4 - N + NO_2 - N + NO_3 - N$

FIGURE IV-8
TEMPERATURE EFFECTS ON NITROGEN
TAKEN UP BY SEDIMENTS

(a)

(b)
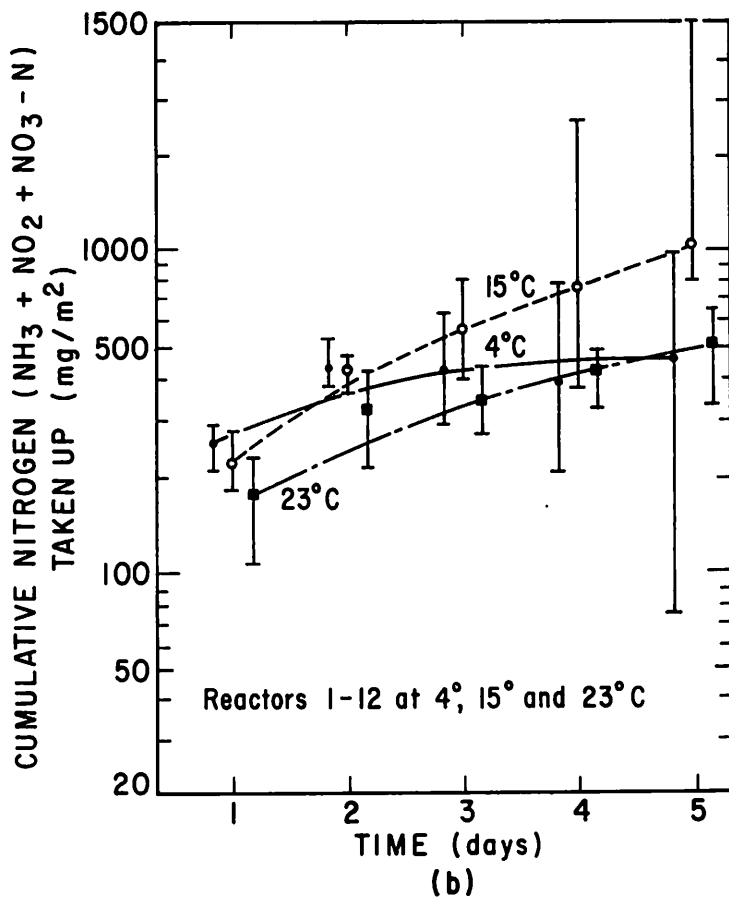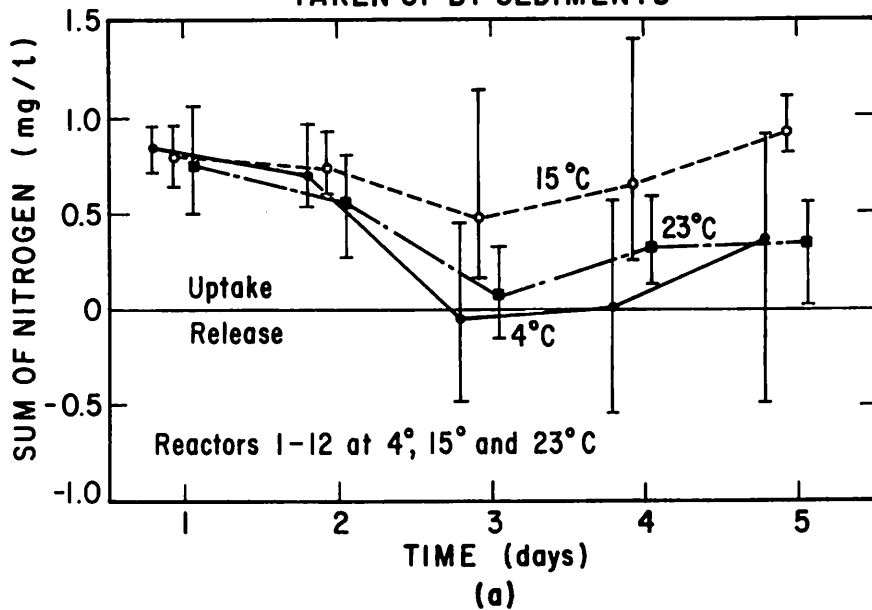
TABLE IV-5

TEMPERATURE EFFECTS[2] ON UPTAKE RATES OF NITROGEN BY SEDIMENTS

| Reactor Temperature (°C) | Time (days) | Nitrogen[1] Uptake Rates | | |
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
4	1	210-287	258	
	2	189-257	217	
	3	98-203	140	
	4	52-142	83	
	5	15-137	70	
15	1	186-270	224	
	2	180-230	211	
	3	130-260	186	
	4	94-290	182	
	5	156-280	203	
23	1	119-228	175	
	2	105-213	158	
	3	92-144	114	
	4	79-123	105	
	5		84	
All Temperatures	1			219
	2			195
	3			147
	4			123
	5			119

[1] Nitrogen = $NH_4 - N + NO_2 - N + NO_3 - N$

[2] Effects for the three temperatures were derived from reactors operated at the three salinities of 0 ppt, 10 ppt, and 20 ppt.

Phosphorus

The effect of temperature on phosphorus release is shown in Figure IV-9 and Table IV-6. Temperature effects were small and the initial unequal concentrations became equal by the third day. By the fifth day, the $15^{\circ}C$ reactors were at equilibrium, the $4^{\circ}C$ reactors were at very low concentrations, and the $23^{\circ}C$ reactors were still releasing at a fairly steady rate. The mass of phosphorus released was very low for all temperature conditions and the $15^{\circ}C$ reactor curve was nearly zero. The main mechanism affecting differential phosphorus release appeared to be different soil characteristics and nutrient contents of the various reactors.

The effect of temperature on phosphorus uptake is shown in Figure IV-10. Some temperature effect is evident as indicated by the higher uptake in the $23^{\circ}C$ reactors. The biomass present in the plexiglas reactors may have caused the $23^{\circ}C$ and $4^{\circ}C$ reactors to follow the classic phosphorus leaching versus uptake response; that is, high uptake rates of phosphorus by a sediment may be indicative of a low release rate by the same sediment. Comparison of Figures IV-9a and IV-10a reveal this pattern was found in the $4^{\circ}C$ and 23° reactors, but the $15^{\circ}C$ reactors did not follow this pattern. Temperature effects on mass of phosphorus taken up appear to be small.

Salinity Effects

The same graphical presentation used for temperature effects was used to compare the effects of salinities on the uptake and release of nutrients. The twelve reactors were grouped according to the salinity conditions of influent waters, and nutrient exchange rates were determined. It was realized that this analysis masked the temperature effects on the release and uptake rates for reactors operated at different temperatures.

Nitrogen

Salinity effects on the release of nitrogen is depicted in Figure IV-11. A salinity effect is not clear, but it is apparent that the

FIGURE IV-9
TEMPERATURE EFFECTS ON PHOSPHORUS
LEACHED FROM SEDIMENTS
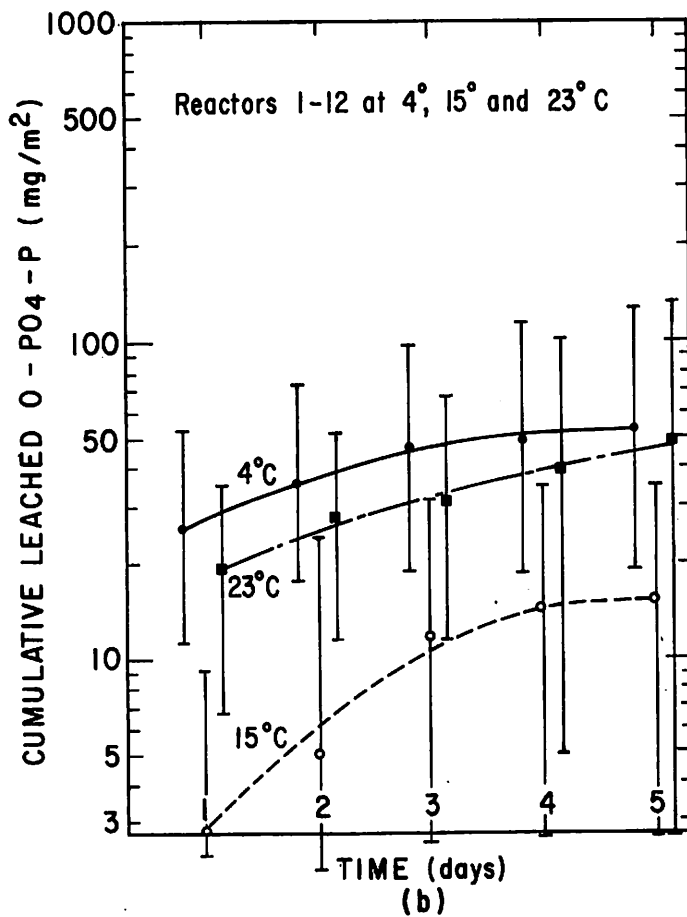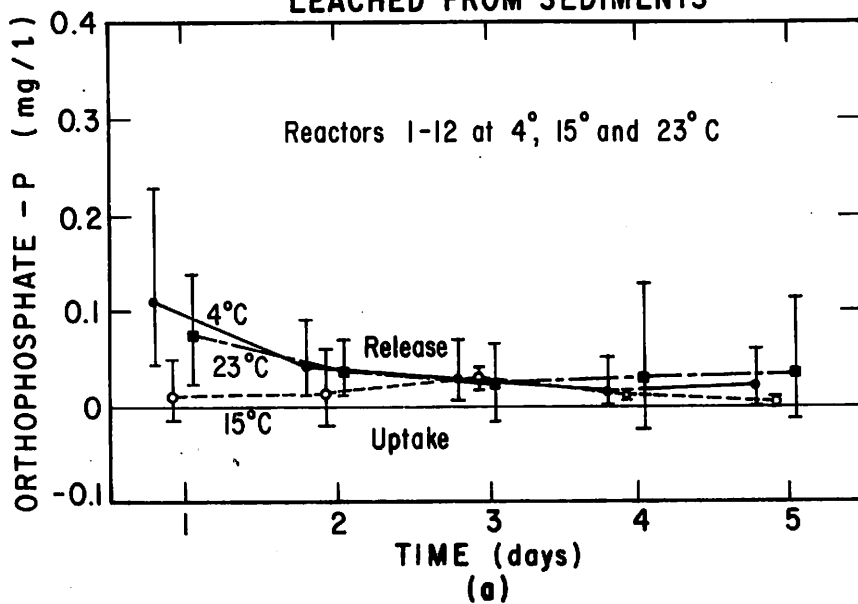
TABLE IV-6

TEMPERATURE EFFECTS[1] ON LEACHING RATES OF PHOSPHORUS FROM SEDIMENTS

Reactor Temperature (°C)	Time (days)	Phosphorus Leaching Rates		
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
4	1	15-53	26	
	2	9-37	18	
	3	6-32	15	
	4	5-28	13	
	5	4-25	11	
15	1	(-) 3- 9	2	
	2	(-) 4-12	3	
	3	2-11	6	
	4	2- 9	5	
	5	2- 7	4	
23	1	7-35	19	
	2	6-26	14	
	3	4-23	11	
	4	2-25	10	
	5	0-26	10	
All Temperatures	1			16
	2			12
	3			11
	4			9
	5			8

[1] Effects for the three temperatures were derived from reactors operated at the three salinities of 0 ppt, 10 ppt, and 20 ppt.

FIGURE IV-10
TEMPERATURE EFFECTS ON PHOSPHORUS
TAKEN UP BY SEDIMENTS
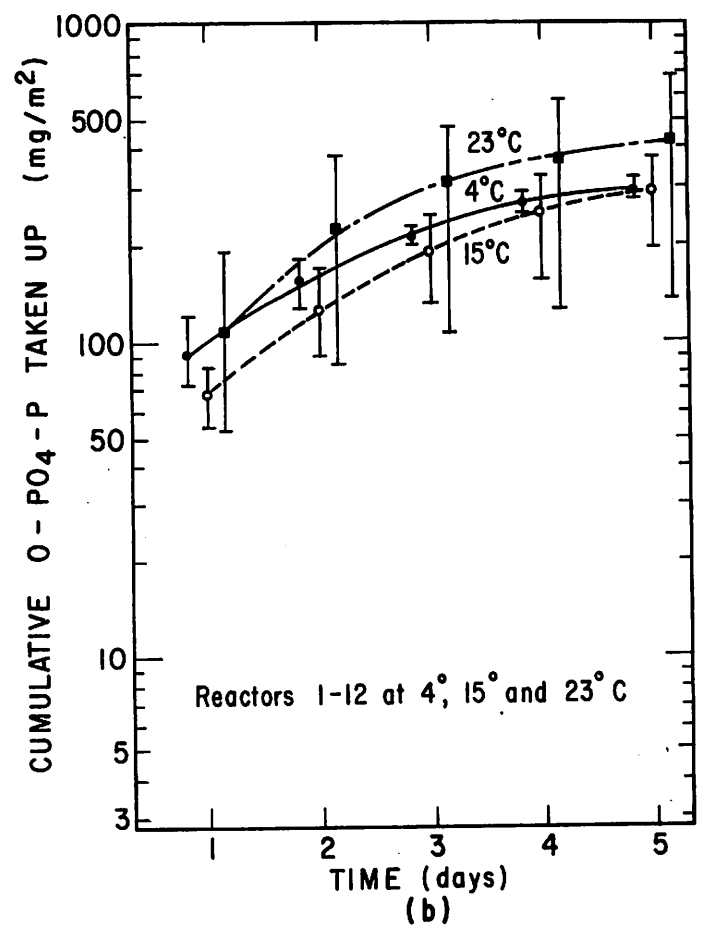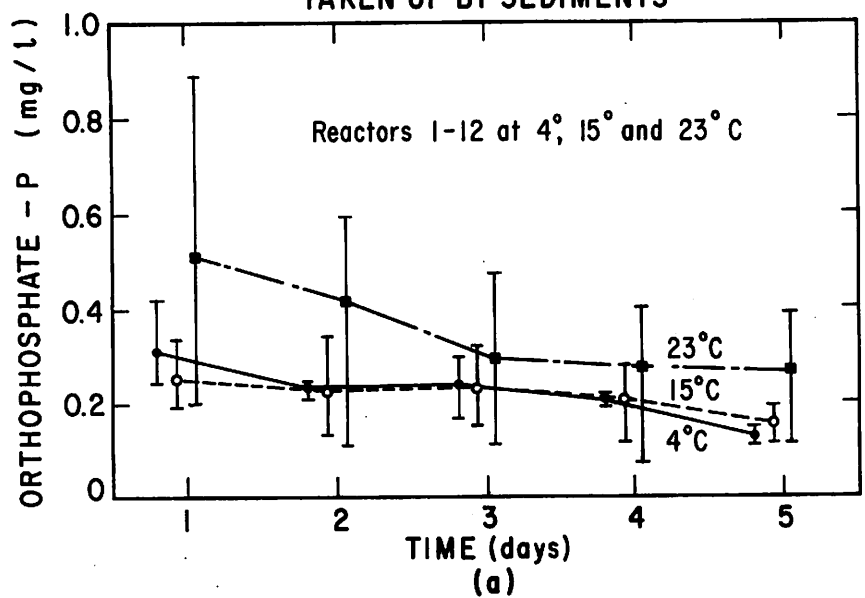
TABLE IV-7

TEMPERATURE EFFECTS[1] ON UPTAKE RATES
OF PHOSPHORUS BY SEDIMENTS

| Reactor Temperature (°C) | Time (days) | Phosphorus Uptake Rates | | |
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
4	1	75-121	92	
	2	67- 92	76	
	3	67- 75	70	
	4	64- 70	66	
	5	56- 63	59	
15	1	53- 83	68	
	2	45- 84	65	
	3	44- 83	65	
	4	41- 80	62	
	5	40- 74	59	
23	1	53-193	116	
	2	42-186	113	
	3	37-167	101	
	4	32-145	94	
	5	26-134	87	
All Temperatures	1			92
	2			85
	3			79
	4			74
	5			68

[1] Effects for the three temperatures were derived from reactors operated at the three salinities of 0 ppt, 10 ppt, and 20 ppt.

FIGURE IV-II
SALINITY EFFECTS ON NITROGEN
LEACHED FROM SEDIMENTS
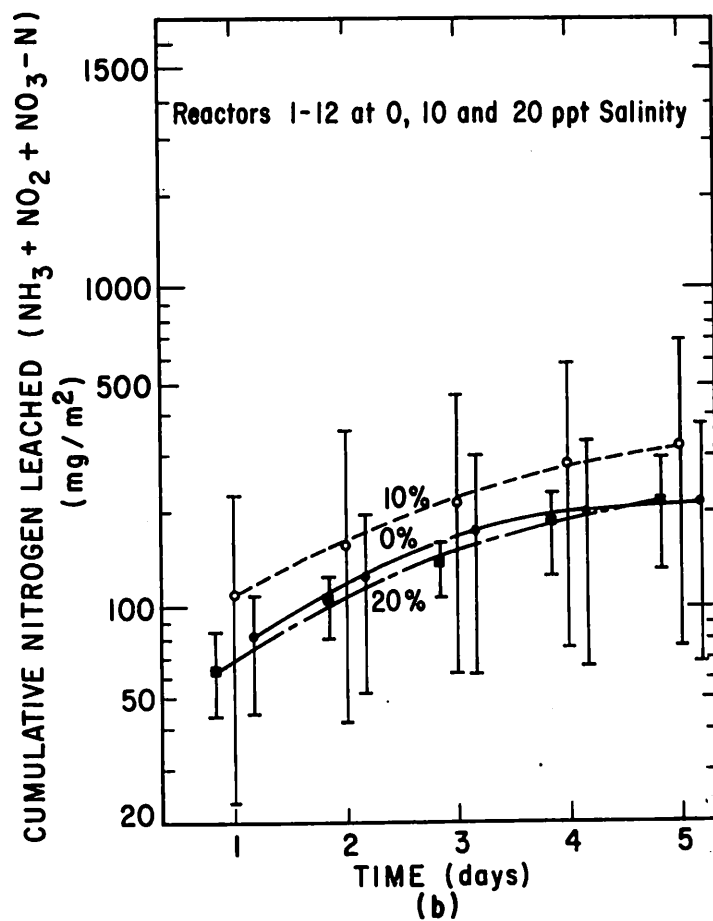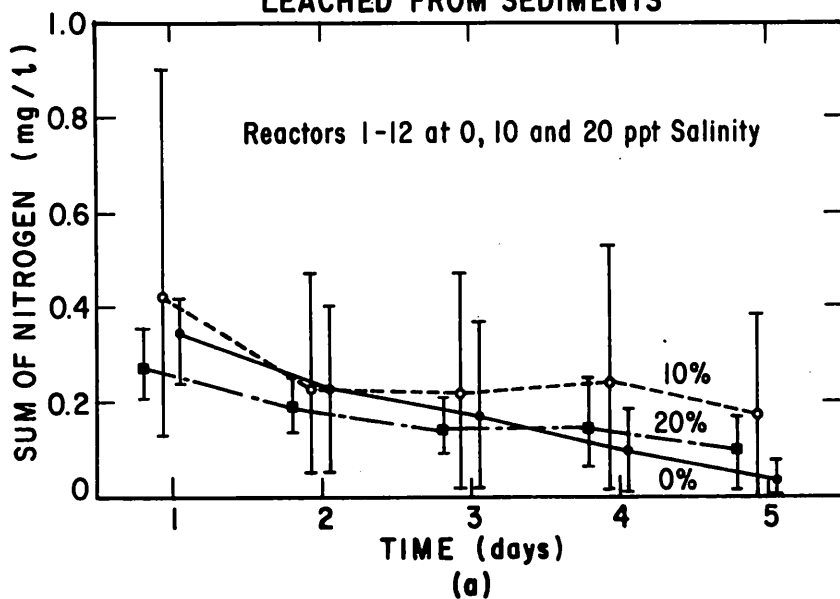
greatest exchange was found in the 10 ppt salinity with lesser rates in the 20 and 0 ppt salinities. The mechanism which may have caused the difference in salinity effects was ammonification and mineralization due to the greater accumulation of the biomass in the 10 ppt reactors at $23^{\circ}C$. Nitrogen release rates through the five-day leaching period at the three leaching salinities are tabulated in Table IV-8.

The effects of salinity on nitrogen uptake are shown in Figure IV-12 and in Table IV-9. The initial uptake mechanism was probably sorption and biomass uptake because initially the greatest amount of uptake was in the biologically active sediments which sorbed large quantities of nitrogen at all three salinities. From day two on, ammonification and nitrification produced equilibrium conditions for the 10 and 20 ppt reactors and the release of nitrogen for a short time by the 10 ppt reactors.

Phosphorus

Salinity effects on phosphorus release are shown in Figure IV-13 and Table IV-10. These results indicated that salinity effects were not quantitatively significant. One mechanism which appeared to cause salinity effects was the biological or chemical oxidation blockage of phosphorus release at the sediment-water interface (Fillos et al., 1975). Under aerobic conditions the overlying water concentrations due to release were low as expected. Another mechanism could be the uptake of phosphorus by the biota present in the reactors, especially the plexiglas reactors at $23^{\circ}C$.

The effects of salinity on phosphorus taken up by the sediments is shown in Figure IV-14 and Table IV-11. Some marked differences were noted which were most likely due to the biota in the 10 and 20 ppt salinity reactors at $23^{\circ}C$. The probable mechanisms involved were absorption (or uptake) by the biota and adsorption by the sediment.

TABLE IV-8

SALINITY EFFECTS ON LEACHING RATES
OF NITROGEN FROM SEDIMENTS

| Reactor Salinity (ppt) | Time (days) | Nitrogen Leaching Rates | | |
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
0	1	46-114	83	
	2	29- 99	69	
	3	21- 98	60	
	4	17- 86	51	
	5	13- 72	42	
10	1	25-227	108	
	2	24-175	84	
	3	21-153	73	
	4	19-148	70	
	5	16 138	65	
20	1	46- 82	64	
	2	42- 72	55	
	3	36- 58	48	
	4	31- 58	45	
	5	25- 55	41	
All Salinities	1			85
	2			70
	3			60
	4			55
	5			50

FIGURE IV-12
SALINITY EFFECTS ON NITROGEN
TAKEN UP BY SEDIMENTS
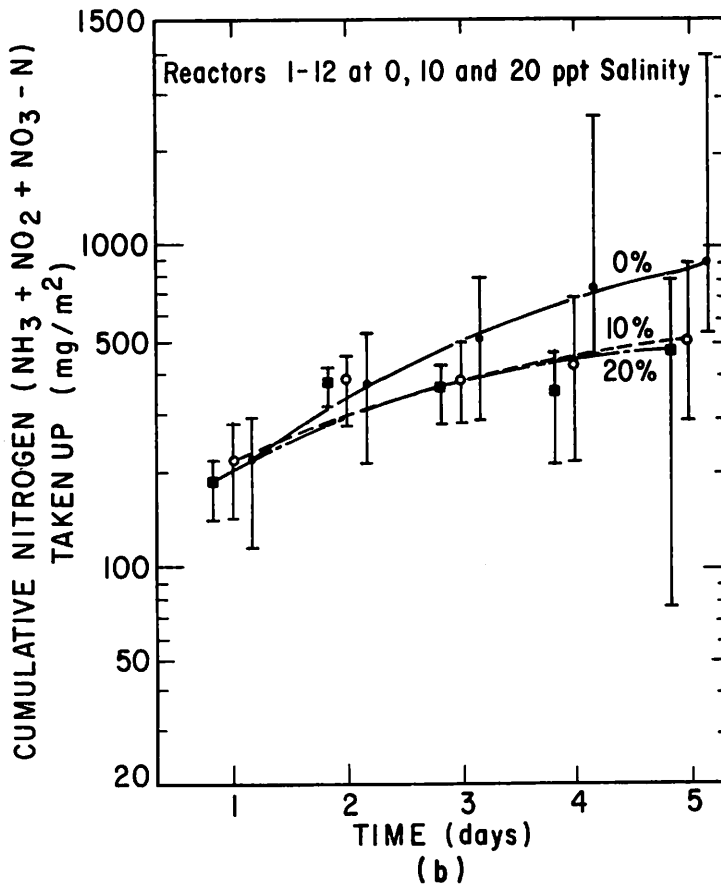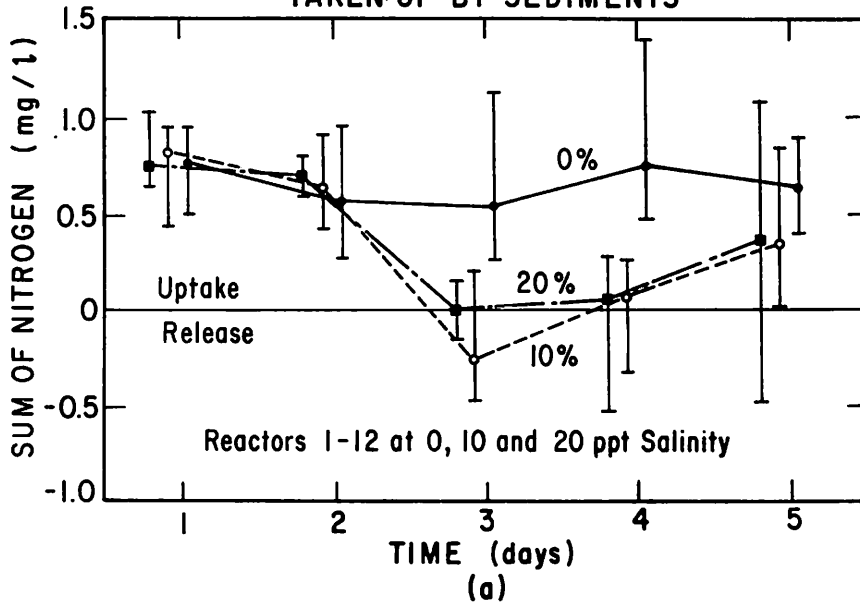
TABLE IV-9

SALINITY EFFECTS ON UPTAKE RATES
OF NITROGEN BY SEDIMENTS

| Reactor Salinity (ppt) | Time (days) | Nitrogen Uptake Rates | | |
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
0	1	119-287	219	
	2	105-257	182	
	3	94-260	170	
	4	109-290	165	
	5	108-280	163	
10	1	146-276	217	
	2	136-224	195	
	3	92-167	125	
	4	54-163	105	
	5	58-172	101	
20	1	145-213	189	
	2	156-204	182	
	3	93-138	120	
	4	52-115	87	
	5	15-156	94	
All Salinities	1			208
	2			186
	3			138
	4			119
	5			119

FIGURE IV-13
SALINITY EFFECTS ON PHOSPHORUS
LEACHED FROM SEDIMENTS

IV-29
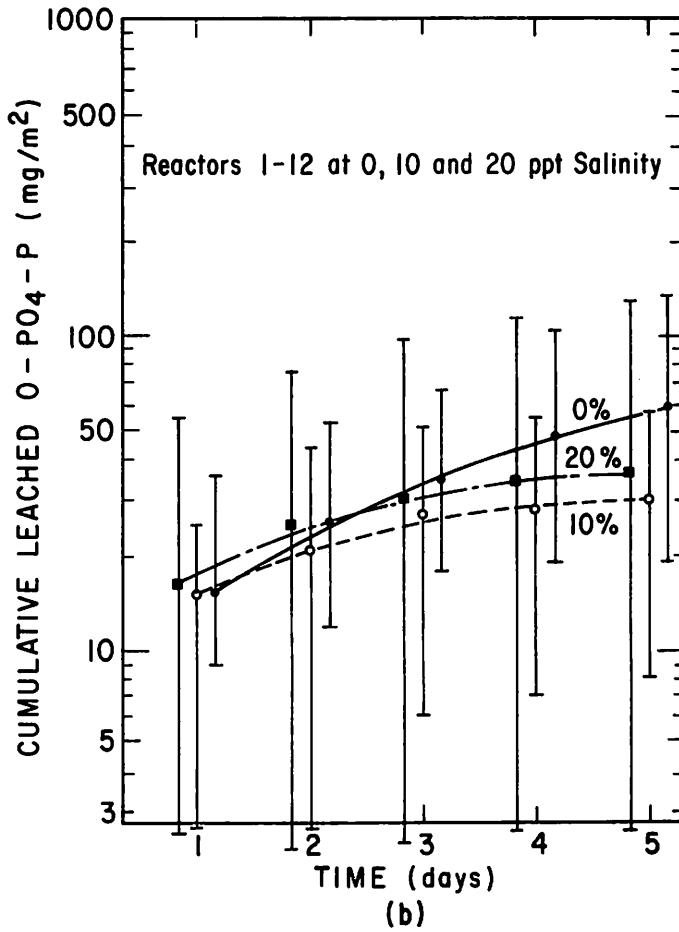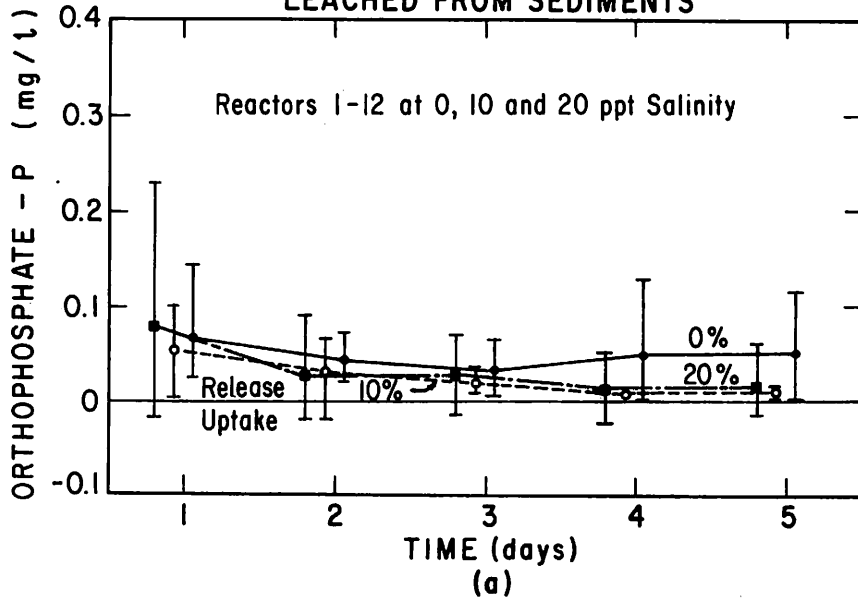
TABLE IV-10

SALINITY EFFECTS ON LEACHING RATES
OF PHOSPHORUS FROM SEDIMENTS

| Reactor Salinity (ppt) | Time (days) | Phosphorus Leaching Rates | | |
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
0	1	7- 35	16	
	2	6- 26	13	
	3	6- 23	12	
	4	5- 26	12	
	5	4- 26	12	
10	1	1- 26	15	
	2	1- 22	11	
	3	2- 27	9	
	4	2- 18	7	
	5	2- 11	6	
20	1	(-) 3- 53	19	
	2	(-) 4- 37	13	
	3	4- 32	12	
	4	2- 28	10	
	5	0- 25	8	
All Salinities	1			17
	2			12
	3			11
	4			10
	5			9

FIGURE IV-14
SALINITY EFFECTS ON PHOSPHORUS
TAKEN UP BY SEDIMENTS

Reactors 1-12 at 0, 10 and 20 ppt Salinity

(a)

Reactors 1-12 at 0, 10 and 20 ppt Salinity

(b)
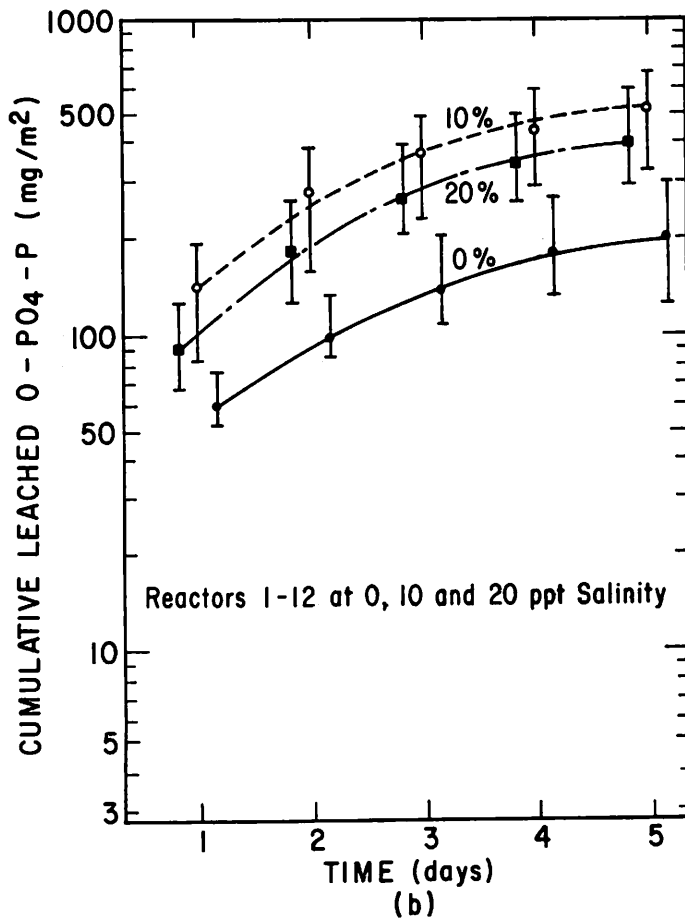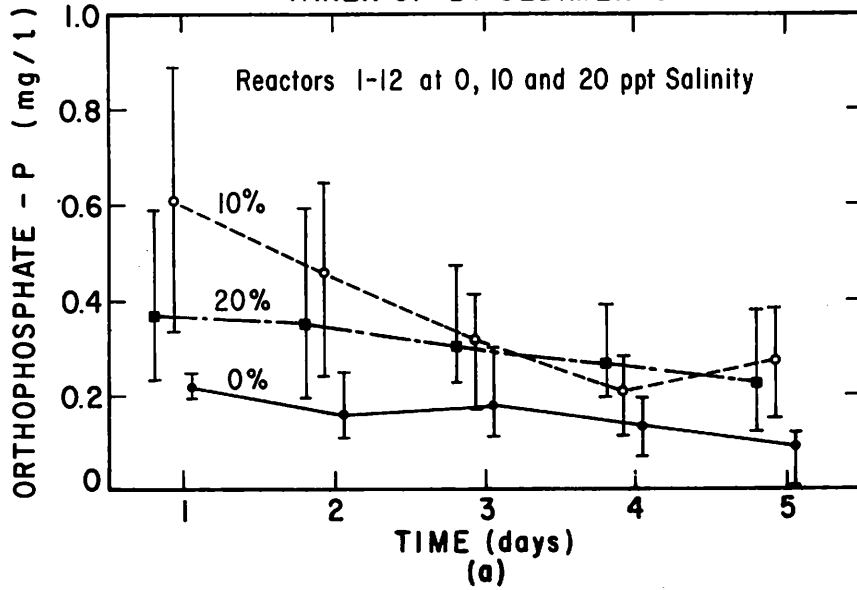
TABLE IV-11

SALINITY EFFECTS ON UPTAKE RATES
OF PHOSPHORUS BY SEDIMENTS

Reactor Salinity (ppt)	Time (days)	Phosphorus Uptake Rates		
		Range $(mg/m^2/d)$	Average $(mg/m^2/d)$	Daily Average $(mg/m^2/d)$
0	1	53- 75	59	
	2	42- 67	49	
	3	37- 67	47	
	4	32- 64	44	
	5	26- 56	40	
10	1	83-193	145	
	2	84-186	136	
	3	83-167	120	
	4	70-145	110	
	5	63-134	101	
20	1	67-124	80	
	2	66-134	90	
	3	67-131	87	
	4	64-123	83	
	5	57-117	78	
All Salinities	1			98
	2			92
	3			85
	4			79
	5			73

CHAPTER V

DISCUSSION

INTRODUCTION

The exchange of nitrogen and phosphorus between the marsh sediments and overlying water has been investigated to determine the rates of exchange and the effects of temperature and salinity on these rates. It was found that release and uptake do occur between the sediments and overlying waters, that temperature and salinity influence those rates somewhat, and that organisms (bacteria and plants) may also exert some influences on these rates.

In order for physical (sorption-desorption) nutrient exchange to occur, a concentration gradient must exist between the sediment and the overlying waters. Factors affecting the physical exchange rates include diffusion in the sediment interstitial water, mixing of water overlying the sediment, flow characteristics, diurnal effects, seasonal changes, and others; these factors cause nutrient concentrations to change continuously in sediment and overlying waters. Interacting with these physical factors acting near the water-sediment interface are plants, animals, bacteria, and so forth. It is apparent that steady-state conditions seldom exist at the sediment-water interface. Even with these complexities, the portions of the marsh system transplanted into the constantly-stirred, flow-through reactors in the laboratory nevertheless appeared to reproduce the field conditions. The major variable, however, was the difference in replicate microcosm sediment characteristics. These variable sediment characteristics, in order of significance, were: organic matter content, available nitrogen and phosphorus, and indigenous biomass. This problem was apparent in the analysis of exchange rate data as well as in the appearance of the sediment. Nevertheless, the results obtained indicated evidence of temperature and salinity effects.

NUTRIENT EXCHANGE BETWEEN WATER AND SEDIMENTS

A summary table of leaching and uptake rates for nitrogen and phosphorus at various temperature and salinity conditions was assembled from the results for reference purposes. Rates at one, three, and five days are combined in Table V-1.

Nitrogen Exchange

Release.

Nitrogen may be released at the sediment-water interface as detritus is decomposed. Under anoxic conditions, the mineralization of nitrogen takes place at a greater rate than under aerated conditions (Sawyer et al., 1967). High nitrogen levels in the sediment interstitial waters may produce a concentration gradient between the sediment and the overlying water which will result in nitrogen transport to the overlying waters by diffusion. Several indirect effects on the sediment-water interchange occur such as change in pH, oxygen consumption, clay sorption of organic nitrogen and others (Keeney, 1973). Information on temperature and salinity effects on nitrogen release was not found in the literature.

From an analysis of the results of this study, it appeared that significant differences in mineralization rates were caused by temperature since nitrogen was released at $23^{\circ}C$ at almost twice the rate as at $4^{\circ}C$ using rates at five days.

Salinity effects on nitrogen release indicated that the organisms which grew especially well in those reactors with 10 ppt salinity exerted a major influence on the release rates. The rate differences were significant as the 10 ppt salinity release rate of 65 $mg/m^2/day$ was fifty percent greater than the 0 and 20 ppt salinity release rates of 42 and 41 $mg/m^2/day$ of nitrogen, respectively.

Uptake

The uptake of nitrogen by the sediments is primarily due to sorption by the sediment and to the organisms present. When enriched nitrogen

TABLE V-1

TEMPERATURE[1] AND SALINITY[2] EFFECTS ON LEACHING
AND UPTAKE RATES OF NUTRIENTS

Parameter	Time (days)	Nitrogen		Phosphorus	
		Leaching $(mg/m^2/d)$	Uptake $(mg/m^2/d)$	Leaching $(mg/m^2/d)$	Uptake $(mg/m^2/d)$
Temperature (°C)					
4	1	75	258	26	92
	3	45	140	15	70
	5	30	70	11	59
15	1	39	224	2	68
	3	26	186	6	65
	5	18	203	4	59
23	1	113	175	19	116
	3	85	114	11	101
	5	74	84	10	87
Salinity (ppt)					
0	1	83	219	16	59
	3	60	170	12	47
	5	42	163	12	40
10	1	108	217	15	145
	3	73	125	9	120
	5	65	101	6	101
20	1	64	189	19	90
	3	48	120	12	87
	5	41	94	8	78

[1] Effects for the three temperatures were derived from reactors operated at 0 ppt, 10 ppt, and 20 ppt salinities.

[2] Effects for the three salinities were derived from reactors operated at 4°, 15°, and 23°C temperatures.

conditions exist in the overlying waters, nitrogen diffusion occurs into the sediments to bring about equilibrium conditions. Information on temperature effects on nitrogen uptake pertinent to this investigation was not mentioned in the literature.

Results of these experiments indicated only minor temperature effects on nitrogen uptake. In comparing the nitrogen release rates with those experienced during uptake, it was found that both rates were quite different as might be expected because of the influent conditions imposed, but those reactors with high sediment organic matter released at higher rates than other reactors and took up nitrogen at lower rates than other reactors. The overall mean nitrogen release rate at five days was 41 $mg/m^2/day$ compared to that of uptake at 119 $mg/m^2/day$ of nitrogen in the organically rich sediments. The organically poor 15°C reactor group showed only 18 $mg/m^2/day$ of nitrogen released while the uptake rate was (high for the three temperature groups) 203 $mg/m^2/day$ of nitrogen, all at the five day point.

The salinity effects on nitrogen uptake was shown by data analysis to be masked by the organisms present, especially, in the 20 ppt salinity reactors. After three days, conditions in the 20 ppt and 10 ppt salinity reactors indicated that mineralization was occurring in the more bacterially active reactors. At the same time, the least biologically active reactors (0 ppt salinity) continued to take up nitrogen. The results of salinity effects on uptake rates at five days were as follows: 0 ppt salinity, 163 $mg/m^2/day$; 10 ppt salinity, 101 $mg/m^2/day$; and 20 ppt salinity, 94 $mg/m^2/day$ of nitrogen.

Phosphorus Exchange

Release

Phosphorus is released from the sediment primarily by desorption into interstitial waters and diffusion into the overlying waters. Release also occurs due to microbial decomposition of detritus at the sediment-water interface.

Salinity effects on the physical (sorption-desorption) release rates
of phosphorus were masked by the organisms at the sediment surface.
The more biologically active reactors had lower release rates as follows:
0 ppt salinity, 12 mg/m^2/day; 20 ppt salinity, 8 mg/m^2/day; and 10 ppt
salinity, 6 mg/m^2/day of phosphorus over the five day period. The 10
ppt salinity reactors contained an abundance of plants apparently adapted
to brackish water conditions which took up phosphorus as it was released
by other mechanisms, thus lowering the net release rate.

Uptake

Sorption is the primary mechanism for uptake of inorganic phosphorus
by the sediment-water system. It has also been observed that bacteria
have the ability to store phosphorus (Hayes and Phillips, 1958), thus
bacteria in the sediment may take up and store phosphorus temporarily.
Since the transport of phosphorus and other materials between the sedi-
ment interstitial water and overlying water depend on rates of diffusion
and extent of mixing action (Lee, 1970), these must also be added to
physical sorption and biological activity as controlling factors in phos-
phorus mobility.

Uptake rates for phosphorus in this experiment were not found to be
affected by temperature. The expected opposite rate effect (i.e., high
rate of release reactors show low rate of uptake) was generally observed
except in the 15°C reactors. This deviation may have been related to
stirring-rate differences since precise stirrer rpm was not monitored, or
more likely this was due to the initial nutrient conditions in the sedi-
ments themselves. Rates of uptake for the five day test period were
noted for the temperature-grouped reactors as follows: 23°C, 87 mg/m^2/
day; 15°C, 59 mg/m^2/day; and 4°C, 59,mg/m^2/day of orthophosphate-P.

Salinity conditions did not follow the patterns reported in the litera-
ture of keeping the phosphorus available in the water. In fact, a reverse
pattern was noted and depended on the abundance of organisms in the 10
ppt, 20 ppt, and 0 ppt salinity reactors. Phosphorus appeared to be
taken up more readily in the more biologically active sediments. Uptake
rates were also found to be quite high compared to release rates. This

indicated that, overall, low inorganic phosphorus levels were originally present in the sediment core samples. Uptake rates observed for the five day test period were as follows: 10 ppt salinity, 101 mg/m^2/day; 20 ppt salinity, 78 mg/m^2/day; and 0 ppt salinity, 40 mg/m^2/day of orthophosphate-P.

COMPARISON WITH PREVIOUS RESULTS

The literature contains the results of numerous nutrient exchange experiments concerned with release while few dealt with uptake. The methods utilized in studies reported in the literature are varied with batch water systems used more frequently than continuously-mixed flow-through water systems. In most cases, results obtained have been reported on a mass per volume basis rather than as a mass exchange rate over time for a sediment or bottom area (e.g., Hayes and Phillips, 1958; Austin and Lee, 1973; Porcella et al., 1970; and Odum et al., 1958). In only a few instances have conclusive results been reported concerning environmental factors which may have influenced the exchange rates (e.g., Chen et al., 1972a; Carrit and Goddgal, 1954; Keeney, 1973). A comparison of previous analyses of release and uptake rate data is given below, but studies of brackish water marsh sediment nutrient exchange under different temperature conditions with similar objectives and scope were not found in the literature.

Previous Results

Release Rates

In a recent experiment by Fillos et al. (1975), conducted to determine the release rates of nutrients from river and lake sediments, the release mechanism was investigated under aerobic and anaerobic conditions. Nitrogen release rates for two sediment samples were reported for aerobic conditions as follows:

NITROGEN (for Lake Warner ~5 mg/m^2/hr or
    sediments)   120 mg/m^2/day of ammonia-N

NITROGEN   (for Muddy River $\sim$15 mg/m^2/hr or

                   sediments)   360 mg/m^2/day of ammonia-N

From the same experiment, the release rate for phosphate was reported after ten days under aerobic conditions as follows:

PHOSPHORUS   (for Muddy River $\sim$0.3 mg/m^2/hr or

                   sediments)   7.2 mg/m^2/day of PO$_4$-P

The effect of simulated benthal deposits on nutrient budget was also studied by Fillos et al. (1972) under both aerobic and anaerobic conditions. Nitrogen and phosphorus release rates were reported for aerobic conditions as follows:

PHOSPHORUS   (for relatively aged   3 mg/m^2/day of PO$_4$-P

                   sediments at 4 months)

NITROGEN   (for relatively aged   62 mg/m^2/day of ammonia-N

                   sediments at 4 months)

Uptake Rates

Although rates of nitrite mineralization were reported by Graetz et al. (1973) in a study of lake sediment-water systems, ammonia uptake investigations were not reported in the literature. Neither did the literature contain information on phosphorus uptake that was useful for comparison with the studies in this investigation.

Comparison

Overall the results of this study indicated high phosphorus uptake rates and extremely low release rates. This was expected and was reported in the literature by Williams (1970). The overall high uptake rates indicated the sediment phosphorus levels were low and that the sediment had acted as a significant inorganic phosphorus sink. Temperature effects on phosphorus release or uptake were not found to be significant, and salinity effects were related, in reality to biological effects, a feature found by Fillos et al. (1975).

The nitrogen release rates reported by Fillos et al. (1975) for lake and river waters of from 120 to 360 $mg/m^2/day$ of nitrogen were two to four times higher than those found in this investigation. This was most likely due to the source of the benthal deposits used in their tests; the river sediments came from an area near an untreated sewage outfall and the lake deposits came from a eutrophic lake surrounded by farm land. Also their samples were thoroughly mixed prior to the experiment.

In a previous experiment by Fillos et al. (1972), simulated benthal deposits released orthophosphorus at 3 $mg/m^2/day$. This was lower than the 9 $mg/m^2/day$ of phosphorus for five day test period found in these studies; however, the comparisons appeared to be reasonable. From that same study, the nitrogen release rate was reported at 62 $mg/m^2/day$ which compared favorably with the rate found in this investigation of 50 $mg/m^2/day$ at the five day period. The two studies by Fillos gave different results since sediment characteristics were dissimilar; in fact, the earlier experiment made use of a simulated sludge made from a mixture of raw primary wastewater solids and fine sand.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Based on the results of this study, the following conclusions have been drawn.

General

1. The completely-mixed, flow-through, fixed-bed reactors provided an adequate representation of those areas in the field dominated by bare sediments and adequate rate exchange data for salinity and temperature effect analyses.

2. The principal control problem experienced during this investigation was variability of sediment, nutrient, and organic matter content.

3. Generally, salinity effects were masked by biological activity at the sediment-water interface.

Nitrogen

4. Ammonia was taken up by the active sediment layer at about 2.4 times higher rate than it was released (119 mg/m^2/day as compared to 41 mg/m^2/day).

5. Tolerance limit effects of salinity on biomass adaptation influenced the nitrogen exchange rates for both release and uptake of nitrogen. Leaching was directly related to the biomass activity while uptake was inversely proportional to biomass activity.

6. Temperature effects were indicated in nitrogen leaching from the sediment but were not apparent in uptake.

Phosphorus

7. Phosphorus uptake rates by the sediments were high (73 mg/m^2/day of phosphorus) overall while the release rates were low (9 mg/m^2/

day of phosphorus) indicating that phosphorus levels in the active sediment layer were extremely low initially.

8. Tolerance limit effects of salinity on biomass adaptation influenced the phosphorus release from and uptake by the sediments. These leaching effects were inversely proportional to the biomass activity while uptake was directly related to biomass activity.

9. Phosphorus release from the active sediment layer was unaffected by temperature while uptake was affected to some minor amount by temperature conditions.

RECOMMENDATIONS

1. The effects of the initial organic material content of the sediments on release rates of nitrogen, phosphorus, and carbon should be investigated.

2. The sediment core samples should be replicated so that more accurate temperature and salinity effects on nutrient exchange evaluations could be made.

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