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*Estuaries*, Vol. 18, No. 4, Papers from William E. Odum Memorial Symposium. (Dec., 1995), pp. 568-578.

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# Preferential Flow and Segregation of Porewater Solutes in Wetland Sediment

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**ABSTRACT:** Sediment macropores (with effective diameters larger than 100  $\mu\text{m}$ ) comprise 11% of the bulk sediment volume in a tidal freshwater wetland vegetated with *Peltandra virginica*. In order to determine effects of macroporous sediment structure on solute transport, we conducted a solute tracer experiment in the sediment. The effective transport volume ( $\Theta_{\text{eff}}$ , the volume of sediment through which solute was transported normalized to sediment bulk volume) was  $0.15 \text{ cm}^3 \text{ cm}^{-3}$ , which is considerably smaller than the total pore space that is potentially available for transport (porosity of sediment is  $0.63 \text{ cm}^3 \text{ cm}^{-3}$ ). A mean transport time of 13 d was required to flush preferential flow paths in *Peltandra* hummocks; hydrologic turnover of the volumetrically dominant matrix pores ( $0.53 \text{ cm}^3 \text{ cm}^{-3}$ ) was apparently much slower. Based on porewater sampler design and hydrological principles, we suggest that  $\text{N}_2$ -purged tension solution samplers and diffusion equilibrators preferentially sample porewater from macropore and matrix domains, respectively. Dissolved ammonium and orthophosphate concentrations were three-fold higher in matrix pores compared to macropores, which is consistent with our finding that more rapid hydrological flushing occurred in macropores compared to matrix pores. Further evaluation of porewater sampler designs in macroporous sediment is needed to improve studies of hydrologic transport and biogeochemical cycling in wetlands.

## Introduction

Coastal wetlands are hydrologically and chemically 'open' systems that exchange substantial quantities of material and energy with land-margin and estuarine ecosystems (review by Nixon 1980; Bowden et al. 1991; Correll et al. 1992). Much of what has been learned about wetland-estuary chemical exchange comes from measuring net material exchanges in tidal channels or through weirs or flumes on coastal wetland surfaces (Gardner 1975; Valiela et al. 1978; Spurrier and Kjerfve 1988; Childers and Day 1990). Although material exchange studies in creeks or flumes are essential to obtain spatially integrated estimates of wetland-water column exchange, they do not isolate the role

of specific pathways of exchange, such as surface-subsurface hydrologic exchange.

The hydrologic effects of tides extend beyond generating surface flows. Drainage at low tide and evapotranspiration remove porewater; replacement occurs by infiltration of tidal water or precipitation. Diffusive and advective exchange of solutes across the sediment boundary have been estimated from solute concentration gradients, hydraulic head gradients, and estimates of sediment hydraulic conductivity. Diffusion from porewater into surface water is an important pathway of export of dissolved nutrients on the wetland surface (Gardner 1975). At creekbanks, horizontal drainage of porewater exports substantial quantities of dissolved nutrients (Jordan and Correll 1985; Yelverton and Hackney 1986). The studies of Gardner (1975), Bollinger and Moore (1984), and Chambers et al. (1992) are important because the re-

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searchers estimated both diffusive and advective components of surface-subsurface solute exchange, and then compared those estimates with direct measurements. None of the studies could fully account for measured solute exports, leaving unanswered the question of which physical factors are most important in driving surface-subsurface solute exchange. Factors that were unaccounted for in those studies include bioturbation (Sharma et al. 1987), pressure-driven exchange due to surface water flow over boundary irregularities (Shum 1993), and advective drainage from microtopographic features such as hummocks. Vertical solute exchange resulting from regional groundwater flow or evaporation-driven wicking to the sediment surface may also be important (Harvey and Nuttle 1995; Nuttle and Harvey 1995).

#### ROLE OF MACROPORES IN SURFACE-SUBSURFACE SOLUTE EXCHANGE

Biological activity of burrowing organisms and rooting plants creates pores of relatively large diameter ( $>100 \mu\text{m}$ ) in soils and sediment; large pores are distributed within a surrounding matrix of sediment particles and very fine pores that are orders of magnitude smaller. The class of larger pores, referred to as macropores, have a fundamentally different origin in comparison to the much smaller pores (referred to as matrix pores). Macropores can substantially increase saturated and near-saturated hydraulic conductivity of soils. Preferential advection of water through soil macropores is widely recognized to be an important control on solute transport in agricultural, rangeland, and forest soils (Beven and Germann 1982; White 1985; Nielson et al. 1986).

Macropores have frequently been observed in intertidal coastal wetlands (Green and Askew 1965; Frey and Basan 1978). The work of Casey et al. (1986), Hemond and Chen (1990), and Harvey (1993) demonstrated that surface water preferentially infiltrates in macropores. Harvey and Nuttle (1995) showed that downward infiltration fluxes and upward evaporation-driven fluxes in the sediment profile were segregated between macropore and matrix pores respectively. Upward advection and evapoconcentration of solutes in matrix pores had the effect of enhancing diffusion from sediment to surface water when the wetland flooded. Harvey and Nuttle concluded that evaporation-driven 'wicking' of salts to the sediment surface contributed substantially to lowering the average salinity of porewater.

The purpose of the present study was to investigate the role of macroporous sediment in determining subsurface solute transport in a tidal fresh-

water wetland. A solute tracer experiment was conducted to quantify preferential subsurface flow in macropores, and to determine the effect of preferential flow on solute transport time scales and on microscale segregation of porewater solutes between pores of different size. Our results indicated that solutes were transported through a small proportion of the available pore space. The effective transport volume (volume in which transport occurred normalized to the bulk volume of sediment) was  $0.15 \text{ cm}^3 \text{ cm}^{-3}$  compared to a total available pore space of  $0.63 \text{ cm}^3 \text{ cm}^{-3}$ . The effective transport volume compared closely with an independent estimate of macroporosity for this sediment, 0.11, obtained by analyzing intact cores from the same experiment in the laboratory using pressure cell technology (Harvey 1993).

We also found that choice of porewater sampler type affected the determination of dissolved nutrient concentrations, because tension samplers selectively sampled macropores while diffusion equilibrators selectively sampled matrix pores. In this tidal freshwater wetland a valid estimate of advective export of dissolved nutrients depended on our hydrological interpretation. Average concentrations of dissolved nutrients in macropores were multiplied by net horizontal pore waterfluxes to estimate drainage from *Peltandra* hummocks;  $63 \mu\text{moles}\cdot\text{m}^{-2} \text{ d}^{-1}$  and  $49 \mu\text{moles}\cdot\text{m}^{-2} \text{ d}^{-1}$  of ammonium and orthophosphate were exported to surface water in this wetland. Preferential flow through macropores and microscale segregation of solutes in pore networks is likely to be important in many other wetlands; further attention in evaluating porewater sampling biases is warranted.

#### Study Site

The subsurface tracer experiment was conducted in Eagle Bottom marsh, a fringing riverine wetland located on the Chickahominy River near its confluence with the James River on the Virginia coastal plain (Fig. 1). This portion of the Chickahominy River is fresh water in character but still experiences semidiurnal tidal fluctuations in river stage (average tidal range 80 cm). The elevation of the wetland surface is intertidal, and the sediment is flooded twice daily by the Chickahominy River.

The wetland extends 400 m from an upland forested hillslope toward the river. Superimposed on the gentle topographic slope (0.005) is smaller-scale microtopographic variation owing to the hummocky growth form of *Peltandra virginica*. The wetland is unvegetated between hummocks except for late season growth of the grass *Zizania aquatica*. Live roots and dead soil organic matter have created a fibrous organic mat that reaches to a depth

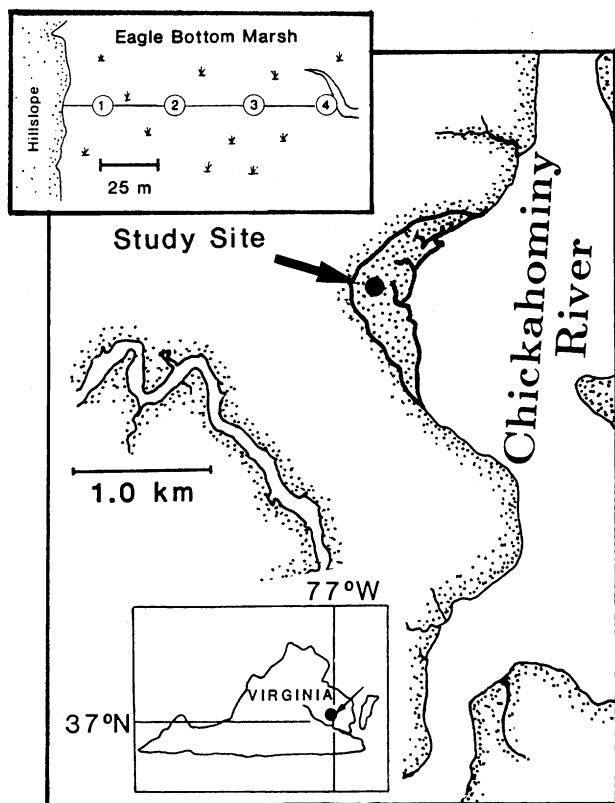


Fig. 1. Eagle Bottom marsh study site. Tracer experimental work was conducted at site 2 in the interior part of the wetland.

of 30 cm in the sediment. Underlying the root zone is a basal mudflat deposit that extends to a depth of 4 m. Beneath the wetland and mudflat deposit is a regionally extensive aquifer that consists of mixed sand and clay.

Water balance measurements and tracer experimentation were conducted during July 1989 in Eagle Bottom marsh at station 2 (Fig. 1), at a study location that was 50 m from the base of the hillside, and about one-third of the distance toward the nearest tidal creek. *Peltandra* hummocks at that location were roughly circular in plan, rising above the surrounding wetland surface an average of 7 cm. Standing water remained ponded in shallow pools between hummocks at low tide. Hummock coverage of the wetland surface was 52%. During the month of July the fraction of time that hummock surfaces were submersed by tidal water was 0.47.

### Methods

#### SEDIMENT POROSITY AND COMPOSITION

Undisturbed sediment samples were obtained by coring using a thin-walled aluminum corer with highly sharpened cutting teeth. Cores up to 60 cm

in length were obtained with minimal compression, transported to the laboratory in PVC liners, and sectioned into 2.5-cm increments. Sediment bulk density was determined by lyophilizing core sections and dividing the dry weight by the original undisturbed volume of the core section. Sediment porosity was computed as the volume of water loss divided by the volume of the core sample. Replicate cores were sectioned and lyophilized to a constant weight for analysis of sediment organic matter content, sediment organic matter density, and sediment mineral density (Faulkner et al. 1989). Sediment macro-organic matter content was determined by thoroughly washing core sections over a 1-mm screened sieve and then lyophilizing the sieved material to a constant weight. A test indicated that weight loss due to lyophilization of cell water in living belowground plant parts did not significantly bias our estimates of average porosity.

#### WATER STORAGE PROPERTIES OF WETLAND SEDIMENT

In addition to saturation storage, compressive (or dilation) storage is sometimes important in peats, including salt-marsh peats in the Northeastern United States (Nuttle et al. 1990). Previous work showed that saturation storage was much greater than compressive storage in this wetland (Harvey 1993). Saturation storage was determined by estimating specific yield ( $S_y$ ), that is, the change in stored water volume in the sediment per unit surface area of sediment per unit change in porewater pressure. Calculations were made based on results of water refill experiments on a large intact sediment core. The core was obtained by twisting a 50 cm length of 30 cm diameter PVC culvert pipe into a *Peltandra* hummock and digging it out. The core was removed to a greenhouse and made watertight on the bottom. The narrow gap between the sediment and PVC container walls was sealed with bentonite, and a manometer was installed through a sideport to measure hydraulic head. The aboveground *Peltandra* plants remained alive during the course of the experiments. Following each addition of a known volume of water to the core, specific yield was calculated as

$$S_y = \frac{\Delta V_w}{A\Delta h} \quad (1)$$

where  $\Delta V_w$  is the volume of water added or released from storage,  $A$  is the surface area, and  $\Delta h$  is the associated change in hydraulic head. Hydraulic head was measured in the field at a sediment depth of 25 cm using piezometers (PVC pipe, 1 cm nominal inside diameter, 10-cm screens at tips).

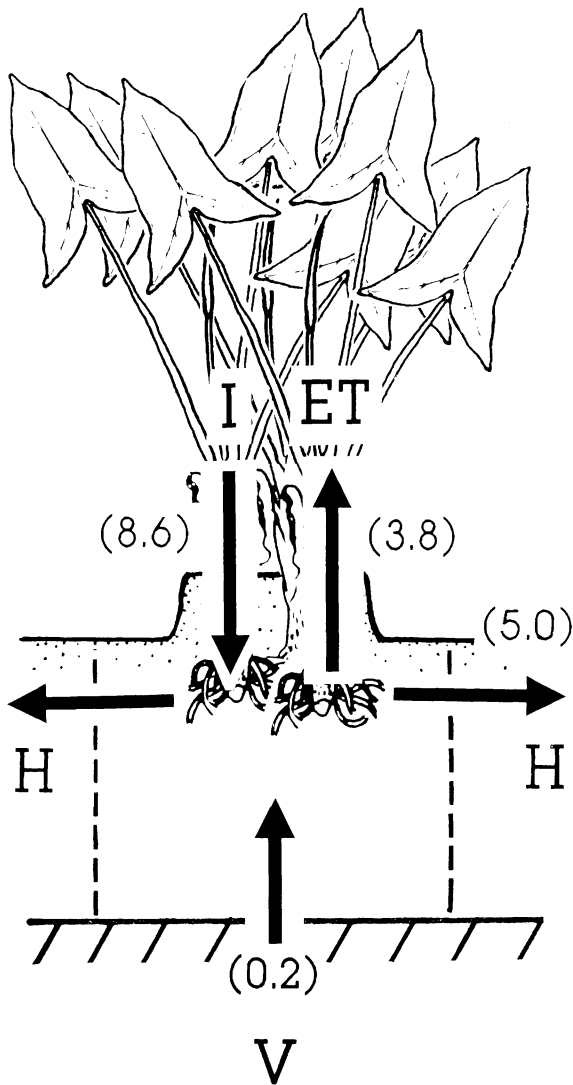


Fig. 2. Area-averaged water balance fluxes in Eagle Bottom marsh. I is infiltration, ET is sediment evapotranspiration, V is exchange with underlying aquifer, and H is the net horizontal flux. Fluxes are reported in  $l^{-1} m^{-2} d^{-1}$ .

#### SEDIMENT WATER BALANCE

The relation between the depth-averaged hydraulic head in the sediment and water balance fluxes is

$$S_y \frac{dh}{dt} = q_I + q_V - q_H^{net} - q_{ET} \pm \epsilon_T \quad (2)$$

where  $q$  is a water flux per unit surface area of wetland,  $\epsilon_T$  represents the total error (i.e., the summed effects of all individual components of random measurement error), and  $h$  and  $S_y$  are hydraulic head and specific yield. Water balance fluxes are defined individually as follows:  $q_b$ , the infiltration flux across the surface;  $q_v$ , the exchange

TABLE 1. Area-averaged sediment water balance: July 1989.

	Pore-water Fluxes ( $l m^{-2} d^{-1}$ )	Error <sup>a</sup> ( $l m^{-2} d^{-1}$ )
$q_H$	5.0	3
$q_{ET}$	3.8	0.8
$q_v$	0.2	2
$q_I$	8.6	4 <sup>b</sup>

<sup>a</sup> Estimated errors are standard deviations.

<sup>b</sup> Total error.

flux with the underlying aquifer;  $q_H^{net}$ , the net horizontal flux;  $q_{ET}$  the sediment evapotranspiration flux.

A time-averaged water balance was determined for the month of July 1989 (during the subsurface tracer experiment), by assuming that the net change in saturation storage for the month was negligible. Although not generalizable to all wetlands, ignoring storage changes over a period of one month is reasonable in this regularly flooded intertidal wetland because tidal inundation resaturates the sediment twice daily. Procedures to estimate each component of the water balance are explained in Appendix A.

The water balance for the experimental site was determined by substituting estimates of  $q_{ET}$ ,  $q_H^{net}$ , and  $q_v$  into Eq. 2. Area-averaged water balance fluxes are shown schematically in Fig. 2 and are reported with error estimates in Table 1. Individual components of error were not estimated directly in this study; we used available criteria (Winter 1981; Field et al. 1992) and personal experience to develop liberal estimates of individual error components. The error estimation procedure assumed that variances of the individual components of random measurement error are independent. The overall error was estimated from the relation

$$\epsilon_T = [\epsilon_v^2 + \epsilon_{ET}^2 + \epsilon_H^2]^{1/2}$$

where  $\epsilon_i$  is one standard deviation associated with the  $i^{th}$  component in the water balance. The infiltration flux,  $q_b$  was estimated as the residual in Eq. 2. Determining the infiltration flux by difference in Eq. 2 was justified because the error term,  $\epsilon_T$ , was reasonably smaller than the residual.

The area-averaged water balance in this hummocky tidal freshwater wetland indicates that porewater was exported from the sediment primarily by horizontal drainage from hummocks and secondarily by evapotranspiration (Fig. 2 and Table 1). Porewater was almost entirely replaced by vertical infiltration of surface water into hummocks; the upward influx of groundwater through the mudflat deposit beneath the wetland was small relative to other fluxes (Table 1).

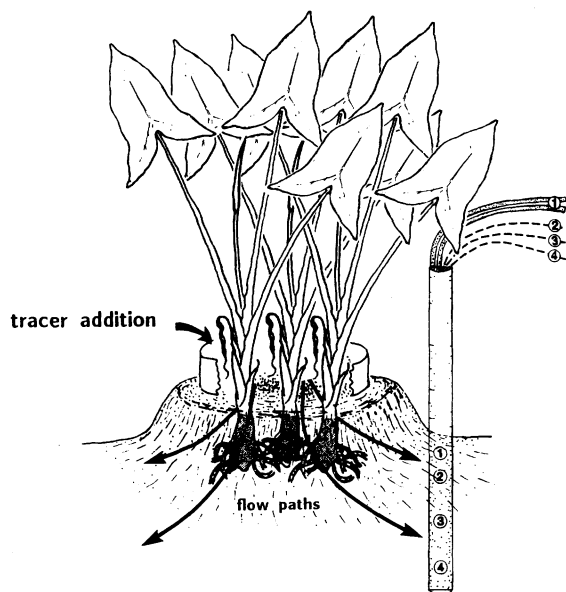


Fig. 3. Schematic illustration of bromide tracer infiltration experiment on 10 *Peltandra* hummocks. Bromide was sampled using multilevel tension samplers (shown) and by coring.

#### SUBSURFACE TRACER EXPERIMENT

Ten infiltration plots were established centrally on surfaces of *Peltandra* hummocks at the experimental site in Eagle Bottom marsh (Fig. 3). Six multilevel solution samplers were installed at the outside margins of four of the experimental plots. Sampling reservoirs were located at 2.5 cm, 5.0 cm, 10.0 cm, and 20.0 cm below the sediment surface. Both a week prior to the experiment and 1 h before tracer was applied, porewater was collected from multilevel samplers to determine the background concentration of bromide in porewater. The tracer experiment began on July 1, 1989; we evenly sprinkled measured volumes of a tracer-labeled solution (approximately 200 ml of 2 M KBr) onto the surface of each plot until the sediment was saturated. The tracer was applied just prior (<30 min) to arrival of advancing river water on a rising tide, thus simulating as closely as possible a natural infiltration event. Porewater was collected at all depths from all samplers at six times following tracer application (0.02 d, 2 d, 5 d, 11 d, 15 d, 20 d, and 27 d). Porewater samples were returned to the laboratory and analyzed for bromide using an ion-specific electrode.

In addition to sampling porewater at hummock margins in tension samplers, we estimated the vertical distribution of tracer in porewater by destructively coring a subset of the infiltration plots. On each sampling date two 5-cm diameter cores and one 10-cm diameter core were collected from designated infiltration plots. The 5-cm cores were

sliced into 2-cm depth increments in the field and transported to the laboratory in sealed bags; 10-cm cores were transported directly to the laboratory for use in pressure cell experiments (Harvey 1993). Bromide concentrations in 5-cm core sections were determined by volumetric inventory following the procedures outlined in Harvey (1993).

#### DISSOLVED NUTRIENT CONCENTRATIONS IN POREWATER

Solute concentrations in porewater were sampled using two methods: tension solution samplers (Litaor 1988) and diffusion equilibrators (Hesslein 1976). Tension solution samplers were constructed of PVC tubes with reservoirs that contacted the sediment at depths ranging between 2.5 cm and 30 cm below the sediment surface. Reservoir intakes were covered with 70- $\mu\text{m}$ , porous polyethylene filters. Prior to sampling, the headspace was flushed with  $\text{N}_2$  to remove all water and replace the headspace in each reservoir with inert gas; a hand vacuum pump was used to apply a suction of 0.3 atm. Porewater was removed after 30 min with a 60-ml syringe, filtered immediately with 0.45- $\mu\text{m}$  pore-size membranes, and placed on ice in a cooler for transfer to the laboratory.

Diffusion equilibrators had triplicate 13-ml reservoirs (2.5-cm diameter intake) drilled in acrylic block and spaced every 4 cm. Equilibrators were prepared by covering all reservoirs with a single sheet of a 0.2- $\mu\text{m}$  membrane filter while all were submerged in  $\text{N}_2$ -purged, deionized water. Equilibrators were removed from the water bath at the study site and emplaced in the sediment. Removal from the sediment occurred after a minimum period of 3 wk. Samples were preserved immediately after collection and placed on ice in a cooler for transfer to the laboratory. All samples from tension samplers and equilibrators were analyzed within 24 h of collection following the standard spectrophotometric methods outlined in Chambers et al. (1992). Electrical conductance was determined on unpreserved samples in the laboratory at a temperature of 25°C.

#### Results and Discussion

##### SEDIMENT CHARACTERISTICS

At the tracer experimental site the average sediment organic matter content in the root zone (top 30 cm of sediment) was 35% by weight. Average bulk density was 0.23 g  $\text{cm}^{-3}$ . Average saturated hydraulic conductivity of the root zone was  $1.2 \times 10^{-3}$  cm  $\text{s}^{-1}$  (Harvey and Odum 1990). Below the top 30 cm of sediment, the underlying basal marsh deposit had a lower organic matter content (12%), a higher bulk density (0.4 g  $\text{cm}^{-3}$ ), and a lower hy-

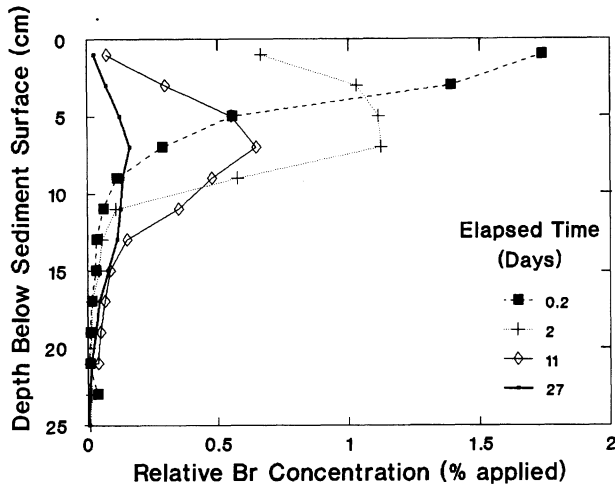


Fig. 4. Relative bromide concentration versus depth in sediment as determined by coring on tracer infiltration plots. Elapsed time is time since tracer application.

draulic conductivity ( $2.0 \times 10^{-5} \text{ cm s}^{-1}$ , Harvey and Odum 1990).

#### SUBSURFACE TRACER MOVEMENT

In total, approximately 80% of the tracer mass released on hummock surfaces was detected by sampling porewater concentrations. Sixty percent was detected by measurement in multilevel samplers at hummock margins, and 20% was detected by volumetric inventory on hummock cores at the conclusion of the experiment. All evidence indicated that tracer initially moved vertically into hummocks and then laterally outward toward hummock margins. Porewater profiles of tracer concentration indicated that there was no significant downward mobility of tracer below 15 cm (Figs. 4 and 5). Movement of tracer out of hummocks by shallow subsurface flow is consistent with the rapid decline in saturated hydraulic conductivity measured below the root zone in this sediment (Harvey and Odum 1990).

A water balance specifically for *Peltandra* hummocks was needed to analyze tracer experimental data (because solute tracer was introduced on hummock surfaces and was monitored at hummock edges). In particular we needed to estimate the net flux of water through hummocks. Our estimate of the net flux through hummocks is the difference between hummock infiltration and hummock evapotranspiration  $q^*_I - q^*_{ET}$  (superscripts indicate water balance fluxes per unit surface area of hummock, determined by dividing area averaged fluxes by the fraction of hummock coverage). The difference between infiltration and evapotranspiration is the net flow, which moves tracer downward and laterally outward toward

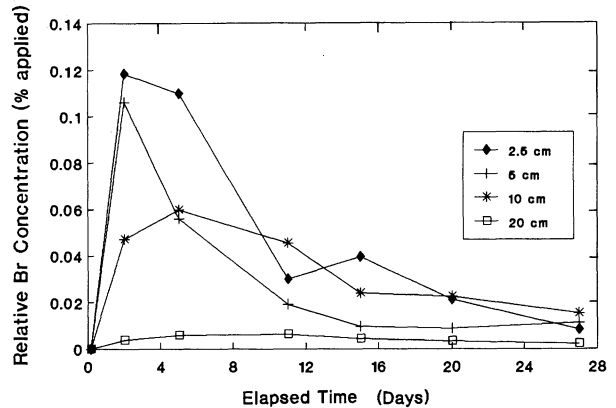


Fig. 5. Bromide tracer concentration measured at a multi-level sampler installed at one tracer infiltration plot. Elapsed time is time since tracer application.

hummock margins. Vertical groundwater flux is negligible in this wetland; therefore the net flux through hummocks essentially represents the net horizontal flux resulting from hummock drainage (Appendix A).

The effective transport volume fraction ( $\Theta_{eff}$ ) is the proportion of the bulk sediment volume through which tracer was transported. Following general approaches outlined in White (1985) and in Hornberger et al. (1990), we used a simple solute model to determine  $\Theta_{eff}$

$$\Theta_{eff} L \frac{dc}{dt} = q^*(c_i - c) \quad (3)$$

where  $c$  is the well-mixed tracer concentration in the sediment,  $c_i$  is the tracer concentration in the infiltration water,  $L$  is the flow path length to the sampler, and  $q^*$  is the net flux of water through hummocks. We assumed that the sudden input of solute tracer by one infiltration event elevated the well-mixed concentration in the sediment to  $c_0$ ; thereafter no input of tracer occurred. For the given assumptions, the concentration response in the sediment is

$$c(t) = c_0 \exp(-tq^*/\Theta_{eff}L) \quad (4)$$

where  $t$  is the elapsed time. Inspection of our tracer concentration data indicated that after quickly reaching a peak, tracer concentrations declined exponentially with time (as implied by Eq. 4). The term  $\Theta_{eff}Lq^{*-1}$  is a mean transport time ( $T$ ) for tracer in the sediment. We estimated mean transport times by determining the elapsed time required for the tracer centroid to reach each sampling depth of multilevel samplers. Effective transport volume fractions were then calculated as  $Tq^*L^{-1}$ . Travel times of tracer from the point of application to the samplers ranged between 11 d and

TABLE 2. Bromide tracer transport-time and effective transport fraction (normalized to bulk sediment volume).

Depth (cm)	Travel-Time (d)	Effective Transport Volume Fraction, $\Theta_{eff}$ ( $\text{cm}^3 \text{ cm}^{-3}$ )
2.5	12.0 $\pm$ 1.4 <sup>a</sup>	0.19 $\pm$ 0.02
5	11.1 $\pm$ 2.6	0.13 $\pm$ 0.03
10	14.6 $\pm$ 1.7	0.14 $\pm$ 0.02
20	13.8 $\pm$ 0.4	0.10 $\pm$ 0.01

<sup>a</sup> Error estimates are standard errors.

15 d. Resulting calculations of effective transport volume fractions in the sediment ranged from 0.10 to 0.19 (Table 2). These transport volumes are considerably smaller than the average porosity (0.63) in the root zone of this sediment.

#### PREFERENTIAL FLOW THROUGH SEDIMENT MACROPORES

Studies of preferential flow in wetland sediments have only recently been undertaken. Casey et al. (1986) showed that surface water with <sup>7</sup>Be, a cosmogenic isotope with a short half-life, was transported to unexpectedly great depths in a wetland soil. Hemond and Chen (1990) found that primarily large pores were stained with a rhodamine dye that had been added to a wetland surface. Harvey (1993) found that tracer in infiltrating water was higher in concentration in macropores compared to matrix pores. The present study quantified the volume fraction through which tracer-labeled infiltration water moved in the sediment ( $\Theta_{eff}$ ). Quantifying  $\Theta_{eff}$  from tracer breakthrough curve characteristics had the advantage of integrating transport processes at the scale of actual flow paths in the sediment.

The principal evidence for preferential flow in this study is determining an effective transport volume fraction (0.15) that was considerably smaller than the porosity (0.63). Our conclusions are strengthened by comparison of results with the direct measurements of solute segregation in cores removed from the site (Harvey 1993). The direct measurement technique utilized 10-cm diameter cores removed from the subset of destructively sampled tracer infiltration plots. In the laboratory pressure cells, porewater was eluted from the intact cores at increasing pressures. At each step tracer concentration in porewater could be related (by the capillary pressure equation) to an effective diameter of the pore network from which the water was mobilized. Measurements were made without compressing or otherwise disturbing the intact core. The pressure cell technique had the advantage of examining solute segregation at a scale where results could be related directly to pore-size distribution and water storage characteristics of the

TABLE 3. Preferential transport in an intertidal wetland sediment: A comparison of independent estimates of effective transport volume fraction,  $\Theta_{eff}$ , and macroporosity,  $\Theta_{macropore}$ . Both estimates are normalized to bulk sediment volume.

Field tracer study, $\Theta_{eff}$	0.15 $\pm$ 0.02 <sup>a</sup>
Laboratory study, $\Theta_{macropore}$	0.11 $\pm$ 0.01 <sup>b</sup>

<sup>a</sup> Error estimates are standard errors.

<sup>b</sup> Estimate from Harvey (1993).

sediment. The breakpoint where drainage of macropores was completed was determined when water yield suddenly decreased rapidly as a function of applied pressure. A macroporosity was calculated from that data,  $\Theta_{macropore}$  (i.e., the volume of macropores normalized with respect to the bulk sediment volume). Independent estimates of preferential flow from field and laboratory studies were compared; both estimates indicate that approximately 10% to 15% of the bulk sediment volume is pore space involved in preferential flow (Table 3).

#### DIFFERENCES IN DISSOLVED NUTRIENTS FROM TENSION SAMPLERS AND EQUILIBRATORS: EVIDENCE FOR SEGREGATION IN MACROPORES AND MATRIX PORES?

Specific conductances were similar in porewater collected using tension samplers and equilibrators. In contrast, dissolved concentrations were approximately threefold higher in samples collected by equilibrators compared to samples collected by tension solution sampling (Fig. 6). Previous researchers have investigated sampling biases of core-squeezing, centrifugation, tension sampling, and diffusion equilibrators. Different techniques were examined in subtidal and coastal wetland sediments by Bolliger et al. (1992), Viel et al. (1991), and Howes et al. (1985). Those investigators found that sampler type only affected dissolved organic carbon concentrations (DOC). DOC was generally higher in water sampled using core-squeezing or centrifugation techniques than in water sampled by diffusion equilibrators or tension solution samplers. Only minor differences were observed in concentrations of other dissolved constituents. Cargnan et al. (1994) recently reported that oxygen trapping in the acrylic of diffusion equilibrators affected some reactive solutes, such as iron, sulfate, and phosphate, but not ammonium. Their data indicated a trend of higher total iron and phosphate in oxygen-affected samplers.

In our study, phosphate concentrations from equilibrators probably were affected to some extent by the oxygen artifact (equilibrators were protected from oxygen for only 24 h before installa-



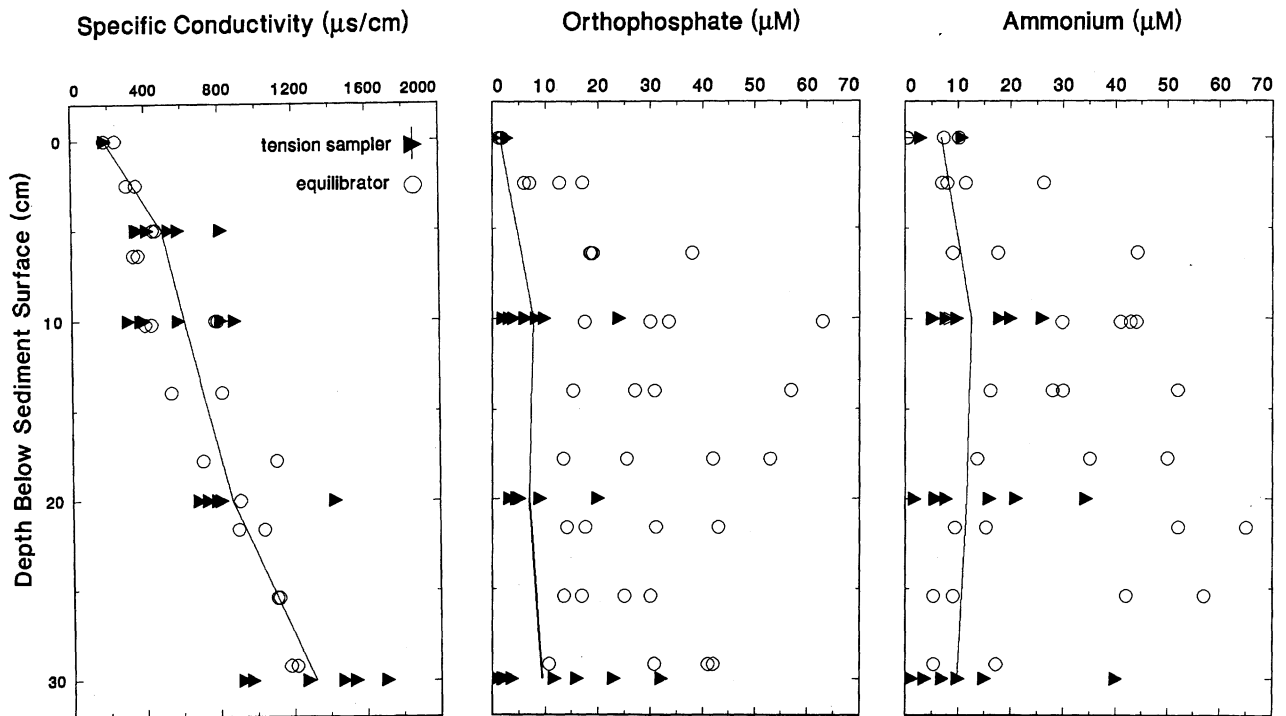


Fig. 6. Sediment depth profiles of specific conductivity, orthophosphate, and ammonium in porewater collected by tension samplers (triangles) and diffusion equilibrators (circles).

tion and were in place for only about a month). Ammonium concentrations were unaffected in the study of Carignan et al. (1994), suggesting that our ammonium data are probably unaffected by oxygen artifacts.

Nutrient concentration differences between sampling techniques most likely resulted from preferential sampling of macropores by tension samplers and matrix pores by equilibrators, respectively. Lower nutrient concentrations in equilibrators probably reflect more rapid hydrological flushing of macropores. Higher nutrient concentrations in matrix pores are probably maintained by mineralization of sediment organic matter, or by equilibrium exchange reactions with a large pool of sorbed nutrients. Specific conductivity did not vary significantly between sampler types, and therefore evapoconcentration could not explain sampling differences. Our interpretation of preferential sampling of macropore and matrix water can be defended based on consideration of sampler design.

Porewater equilibrators work by diffusive exchange of solutes across a filter membrane until the solute chemistry of equilibrated water samples resembles the chemistry of water in the pore spaces with which they are in contact. Because the domain of large pores accounted for only a small proportion of the bulk volume of our sediment (Table

3), diffusion equilibrators are most likely to provide concentrations representative of the volumetrically dominant matrix pores in the sediment.

Tension solution samplers, on the other hand, work by imposing a pressure gradient in the sediment, causing water to flow toward the sampler reservoir from surrounding pores. From theory, the source of porewater to tension sampler reservoirs is expected to be weighted toward the largest wetted pores that contact the sampler. Capillary theory indicates that the possible range of pore sizes that could contribute to flow is bounded at one end by the largest wetted pores and at the other end by pores with an effective diameter that is related to the tension applied in the solution sampler. The pressure cell elution experiments of Harvey (1993) demonstrated that microscale segregation of a solute tracer in this wetland sediment can be characterized by capillary theory. At the low applied tensions in this study ( $<300$  cm  $H_2O$ ) the size range of pores that could contribute flow to the sampler is narrow and in the macropore range.

All of the available information leads us to tentatively conclude that tension solution samplers and equilibrators preferentially sample macropore and matrix porewater concentrations in saturated wetland sediments. We hope that these preliminary results will stimulate more work on prefer-

ential subsurface flow and porewater sampling biases in wetlands.

### Summary

Our tracer experiment showed that advective transport occurs preferentially through the domain of larger pores in the sediment of this intertidal wetland. Using a tracer-based hydrological approach we showed that the volume fraction in which transport occurs constitutes a small proportion (0.15) of the bulk volume of sediment. From a hydrological standpoint, rapid turnover of water in a small proportion of the pore space has potential to introduce variability in porewater solute concentrations at very fine scales. From a methodological standpoint, we suggest that the researcher must be aware of which water type is being sampled. Amongst two typically used procedures, we found that porewater equilibration primarily sampled water from the matrix domain and tension solution samplers collected water primarily from macropores.

Dissolved nutrients varied by threefold in concentration in matrix pores compared to macropores. Investigation of hydrological transport at fine scales provided a basis from which to understand physical controls on microscale solute variability in sediment. From a biogeochemical perspective, finding that specific conductivity was unaffected by preferential flow in this wetland sediment suggested that the pattern of dissolved nutrients must reflect an interaction between the rate of organic matter mineralization and the rate of hydrological flushing in each pore-size region. Furthermore, macropores enhance the advective export of dissolved nutrients to surface water. Further work will determine whether segregated transport and reaction of dissolved nutrients in two pore-size domains enhances the overall reactivity of dissolved nutrients in wetland sediment.

### ACKNOWLEDGMENTS

We wish to express our gratitude to Bill Odum for his guidance and support in wetland research. Partial funding for the research was provided through grants from the Virginia Graduate Marine Consortium/National Oceanic Atmospheric Administration, and National Science Foundation grant BSR-8702333. Additional funding for RMC was provided by United States Department of Agriculture grant #91-37102-6859. The manuscript was improved through the comments of Dave Osgood, Bill Nuttle, and two anonymous reviewers.

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Received for consideration, February 15, 1994

Accepted for publication, May 8, 1995

## Appendix A. Estimation of Area-averaged Sediment Water Balance

The procedure to estimate area-averaged water balance fluxes at the tracer experimental site is explained in this appendix, beginning with the net horizontal water flux. Theoretically, the net horizontal flux in coastal wetlands is affected by local changes in the slope of the wetland water table according to

$$q_H^{\text{net}} = -K \left( \frac{\partial h}{\partial x} + \frac{\partial h}{\partial y} \right), \quad (\text{A-1})$$

where  $h$  is hydraulic head at the water table,  $x$  and  $y$  are horizontal distance coordinates, and overbars indicate average hydraulic gradients (Nuttle and Hemond 1988). Equation A-1 implies that the net horizontal flux is a balance between shallow

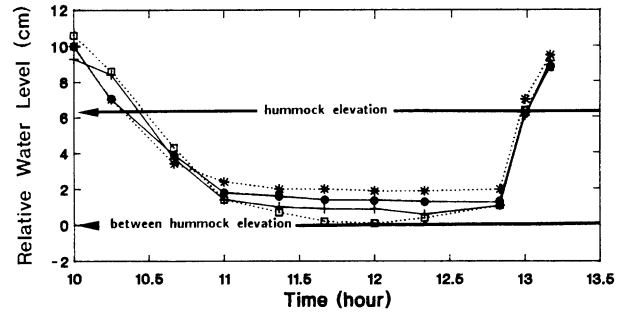


Fig. A-1. Changes in relative water level in piezometers installed within *Pelletandra* hummocks (solid lines) and between *Pelletandra* hummocks (dotted lines) measured over a partial tidal cycle. On the falling tide the water levels in all piezometers decreased to a level below the elevation of hummock surfaces, but the level was similar to the sediment elevation between hummocks.

groundwater fluxes toward a point versus fluxes away from that point. If horizontal outflow from a point exceeds horizontal inflow then the head will decrease locally. Microtopographic features have the potential to vastly increase the net horizontal flux, due to the initially large slope in the water table after the wetland surface is exposed at low tide.

Hydraulic head measurements at our wetland site demonstrated that *Pelletandra* hummocks were microtopographic high points that drain rapidly after exposure of hummocks following tidal submersion (Fig. A-1). We assumed that the component of the net horizontal flux resulting from hummock drainage was much greater than the component due to the small local change in overall wetland surface slope. The net horizontal flux was determined by estimating the rate of water drainage from hummocks, multiplied by the fractional coverage of the wetland surface by hummocks:

$$q_H^{\text{net}} = \lambda \eta (z_s - h_{\text{min}}) S_y \quad (\text{A-2})$$

where  $(z_s - h_{\text{min}})$  is the average difference in elevation between the level of hummock surfaces and the minimum water table elevation at low tide,  $\eta$  is the frequency of tidal inundation,  $d^{-1}$ ,  $\lambda$  is the fractional coverage of the wetland surface by hummocks (0.52), and  $S_y$  is the specific yield.

Total evapotranspiration is the sum of transpiration by *Pelletandra* and other macrophytes, plus evaporation from the exposed sediment at low tide, plus evaporation from standing water on the wetland surface. Total evapotranspiration was assumed to equal potential evapotranspiration (PE) in this wetland, which assumes that evapotranspiration is not limited by the availability of water. We determined PE using the method of Priestly and Taylor (1972):

$$PE = \frac{\alpha_E}{\rho L \Delta + \gamma} (R_N - G) \quad (\text{A-3})$$

where  $R_N$  is the net radiation flux to the surface from above,  $\rho$  is the density of liquid water,  $L$  is the latent heat of vaporization,  $\Delta$  is the rate of change of saturation vapor pressure with air temperature near the ground, and  $\gamma$  is the psychrometric constant.  $G$  is the vertical soil heat flux to the surface, and  $\alpha_E$  is an empirical constant established by Priestly and Taylor.

At the experimental site net radiation was measured 3 m above the ground and air temperature was measured 2 m above the ground at 10-min intervals for the month of July. Computations of PE ignored the soil heat flux because it was found to be a negligible term in the energy balance of another coastal wetland (Nuttle and Hemond 1988). Net radiation measurements were slightly negative at night, corresponding to forma-

tion of dew by condensation. We assumed that PE was zero at night because the Priestly-Taylor method is not considered to be a good predictor of dew formation, and the amount of condensation was probably small.

Our interest was in estimating water loss by transpiration and by evaporation from sediment, which requires that the estimate of total evapotranspiration be reduced by the amount of evaporation that occurred from surface water during high tide. Hussey and Odum (1992) estimated the fraction of total evapotranspiration that is transpiration ( $v$ ) in this wetland as a function of *Peltandra* leaf area. We calculated transpiration by multiplying their estimate of  $v$  for the month of July by our estimate of PE. Surface water evaporation was calculated as PE  $(1-v)$  ( $\alpha$ ), where  $\alpha$  is the fraction of time that hummock surfaces were submersed by tidal water during the 1-mo study period. Our estimate of the total evapotranspiration flux from sediment,  $q_{ET}$ , is the dif-

ference between PE and the estimate of surface water evaporation.

Groundwater discharge from beneath the wetland at our study site was estimated in a previous study (Harvey and Odum 1990). The vertical flux beneath the wetland was calculated using

$$q_v = -K \frac{(\bar{h}_a - \bar{h}_w)}{X} \quad (\text{A-4})$$

where  $h_a$  and  $h_w$  are average hydraulic heads in the aquifer and wetland sediment, respectively, and  $X$  is the distance between the piezometer screen in the aquifer and stratigraphic transition between the aquifer and the wetland sediment with higher hydraulic conductivity. In other wetlands without complicating microtopography, the vertical flux can sometimes be estimated more accurately using the storage-based, statistical-analytic method described by Nuttle and Harvey (1995).

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