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Fluxes of water and solute in a coastal wetland sediment. 2. Effect of macropores on solute exchange with surface water

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Abstract

We investigated interactions between sediment physical structure and solute transport in an intertidal coastal wetland. Two distinct pore-size classes in the sediment were identified. Macropores had effective diameters greater than 100 μm and a normalized volume of 5%; matrix pores had effective diameters smaller than 100 μm and were the volumetrically dominant pore-size class (95%). We found that infiltration and evaporation-driven water fluxes were segregated between macropores and matrix pores, respectively, which had the effect of enhancing diffusive effluxes of chloride from the sediment to surface water. Chloride was highly concentrated relative to seawater in matrix porewater but was comparatively dilute in macropores. Concentration differences in pore-size classes declined with depth until indistinguishable below 10 cm. The segregated chloride distribution can be explained if recharge to the sediment occurred by downward infiltration in macropores and discharge occurred by an upward flux in matrix pores to satisfy evapotranspiration. Without disturbance by the downward infiltration flux in macropores, upward advection of chloride in matrix pores and evapoconcentration increased chloride concentrations in matrix pores to a level well above the concentration in seawater. The resulting high concentrations of chloride in matrix pores induced a large diffusive efflux of chloride into surface water that was sufficient to balance new input of chloride by infiltration of seawater in macropores (0.085 mmol Cl cm^{-2} day^{-1}). Transport models that were constrained by water balance measurements at the field site explained both the exponential form of the vertical distribution of chloride in matrix pores and the rate of change in storage of chloride in sediment porewater over a 1 month period. We conclude that segregation of water and solute fluxes in two pore-size classes strongly influences sediment salinity of coastal wetlands, which has direct bearing on primary productivity of dominant vegetation and on exchange of dissolved nutrients and contaminants between intertidal wetlands and open water.

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1. Introduction

Identifying the hydrological factors that affect water and solute fluxes across wetland interfaces is a fundamental problem in watershed science. The role of wetlands is of special interest, owing to sharp chemical and hydrological gradients at wetland interfaces that affect fluxes and transformations of materials and energy during movement between upland and aquatic ecosystems. Hydrogeologic features of wetlands vary greatly, and this has stimulated solute transport research in a number of physiographic types of wetlands throughout North America, including peatlands (Siegel, 1983; Roulet et al., 1992), swamp and riverine wetlands (Mulholland and Kuenzler, 1979; Mitsch et al., 1979; Johnson et al., 1990), lake margin wetlands (LaBaugh, 1988; Winter and Woo, 1990), and coastal wetlands (Valiela et al., 1978; Correll, 1981; Price and Woo, 1990).

A large number of solute transport studies have been conducted in intertidal wetlands in estuaries and coastal rivers with tidal influence; for example, Bowden et al. (1991), and many other references cited in the review paper by Nixon (1980). That work demonstrated that intertidal wetlands, i.e. wetlands that are flooded periodically by inundation of seawater at high tide, are 'open' chemical systems which exchange substantial quantities of dissolved carbon, nutrients, metals, and radionuclides with surrounding water bodies. Recent studies in coastal wetlands have sought an improved mechanistic understanding of the physical factors that control solute exchange between sediment and surface water (Gardner, 1975; Bollinger and Moore, 1984). Diffusive exchange between sediment and flooding surface water is important, although a number of studies indicate that additional underlying mechanisms must be at work to explain the high rates of solute effluxes from the wetland sediment (Gardner, 1976; Bollinger and Moore, 1984; Casey et al., 1986; Chambers et al., 1992). Morris et al. (1990) argued that determining the factors that affect sediment salinity in coastal wetlands is a critical step toward understanding controls on primary productivity and nutrient cycling in estuaries.

1.1. The role of advection in surface–subsurface solute exchange

Some of the early solute transport models for intertidal coastal wetlands (Casey and Lasaga, 1987; Lord and Church, 1983) adapted their approach from the subtidal sediment interface literature (reviewed by Berner (1980)). The effect of subsurface advection on solute fluxes was usually not considered in those works.

Evapotranspiration is often the most significant water loss from coastal wetland sediments (Hemond and Fifield, 1982); water is replaced by precipitation or by infiltration of flooding estuarine water (Hemond et al., 1984). Over time, sediment salinity is increased owing to evapoconcentration (Chapman, 1960; Casey et al., 1986). New salt is added to the sediment each time a coastal wetland floods by infiltration of seawater. The small horizontal drainage flux at creekbanks is relatively ineffective in removing those salts (Nuttle and Hemond, 1988). Eventually, diffusion or some other export mechanism must balance the continual resupply of salt that occurs by infiltration.

Gardner (1976) made careful mass balance measurements of silica transport in a number of coastal wetlands during recession of ebbing tidal water. Diffusive effluxes far exceeded drainage fluxes; however, the sum of drainage and diffusion still accounted for only a small percentage of the mass balance export measurements. Similarly, Bollinger and Moore (1984) found that diffusion was insufficient to explain measured exports of radium from sediment porewater of a salt marsh sediment into surface water. Other possible mechanisms of salt export include bioturbation (Sharma et al., 1987), root-uptake and release from leaves (Bradley and Morris, 1991), or flushing by advective throughflow of fresh groundwater (Harvey and Odum, 1990; Nuttle and Harvey, 1995).

1.2. Hypothesized effect of macropores on surface–subsurface exchange

The influence of vertical subsurface advection on diffusive solute exchange across the sediment surface has not previously been studied in coastal wetlands. As water flows both upward and downward in the sediment profile, the effect of opposing directions of water fluxes on diffusion needs to be considered. Evaporation-driven advection will transport chloride upward in the profile and increase chloride concentrations near the sediment surface; however, infiltration will flush chloride back down into the sediment and reduce chloride concentrations near the surface. The presence of macropores in the sediment suggests the possibility that water and solute fluxes in opposing directions may be segregated within pore networks of different size.

Soil macropores and their effects on water and solute transport have long been investigated in soils (reviewed by Beven and Germann (1982) and White (1985)), but only recently in wetland sediments. Fine-grained substrates of coastal wetland sediments are often infused with macropores created by organism burrowing and root growth and decay (Green and Askew, 1965). Tracer experiments in coastal wetlands showed that the macroporous sediment structure in these systems has important effects on apparent rates of advective transport (Casey et al., 1986), and on uniformity of the distribution of a solute tracer as a function of effective pore size (Hemond and Chen, 1990; Harvey, 1993).

We hypothesize that vertical fluxes of water and solute in coastal wetlands are segregated by pore size, with infiltration occurring in macropores and upward flow and evaporation occurring in matrix pores. Desaturation occurs during low tide but the porewater tensions achieved during desaturation only exceed the air entry tension for the largest pores in the sediment (Hemond and Chen, 1990; Harvey, 1993); it follows that desaturation should occur only in macropores. In this paper we propose that desaturation in the sediment occurs by imbibition of macropore water into matrix pores, where water is transmitted upward to the sediment surface to replace water lost by evaporation (Fig. 1). Infiltration experiments with tracer-labeled water demonstrated that surface water preferentially infiltrates macropores when the wetland surface floods (Casey et al., 1986; Hemond and Chen, 1990; Harvey, 1993). Our hypothesis must focus on determining whether upward fluxes and evaporation occur only in the matrix pore network. Our reasoning is that the sediment stores much greater quantities of water in matrix pores than in macropores (Harvey, 1993), and
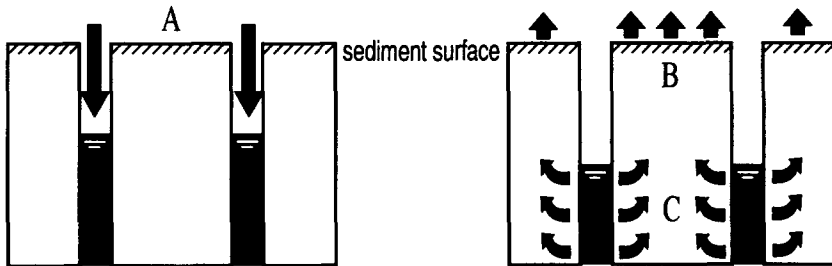
Fig. 1. Conceptual model for segregation of infiltration and evaporation-driven fluxes between macropores and matrix pores. (A) Surface water infiltrates macropores when wetland floods; (B) evaporative water loss at surface is satisfied by withdrawal of macropore water into matrix and upward flow in matrix pores (C).

thus the wetted pore space that is exposed to the atmosphere on the wetland surface at low tide is mostly matrix pores. The evaporative demand should be satisfied by a flux from matrix pores, providing that no severe limitation on the flux is imposed by the hydraulic conductivity of the matrix pores.

Even simplified two-porosity hydrological models are highly parametrized in comparison with available data on sediment hydrological properties at the present wetland site. Our tensiometer measurements in the thin zone of desaturation in this sediment (less than 30 cm) lacked sensitivity to determine vertical hydraulic gradients (Nuttle and Harvey, 1995). In addition, we do not know the hydraulic conductivity of the sediment as a function of pressure and saturation. Without that information we could not rely strictly on hydraulic information to determine whether the upward flux occurred only in matrix pores. We chose instead to test our hypothesis using chloride as an environmental solute tracer for flow in large and small pores. We measured chloride distribution with depth in the sediment in pores of different size; that procedure required intercomparison of sampling methods. A chloride transport model and a field mass balance on chloride in sediment were used to evaluate our hypothesis about flow segregation in pore-size networks. A 'test' of the hypothesis was afforded by comparison of results with transport and mass balance models that were constrained by the water balance at this study site.

2. Study site

The study was conducted in an intertidal coastal wetland in Virginia on the Atlantic side of the Delmarva Peninsula (Fig. 2). The surficial sediment at the study site is a silt loam (Cobb and Smith, 1989), that is approximately 2 m deep, overlying much thicker deposits of beach and marginal marine sediments (Nuttle and Harvey, 1995). Sediment bulk density, porosity, and organic matter content were determined by standard methods (Black et al., 1965; Page et al., 1965; Faulkner et al., 1989). Sediment to 20 cm depth has a bulk density of 1.5 g cm^{-3}, a porosity of 0.42, and an average organic content of 4%. The wetland is vegetated with the short-form of smooth cordgrass, *Spartina alterniflora.*
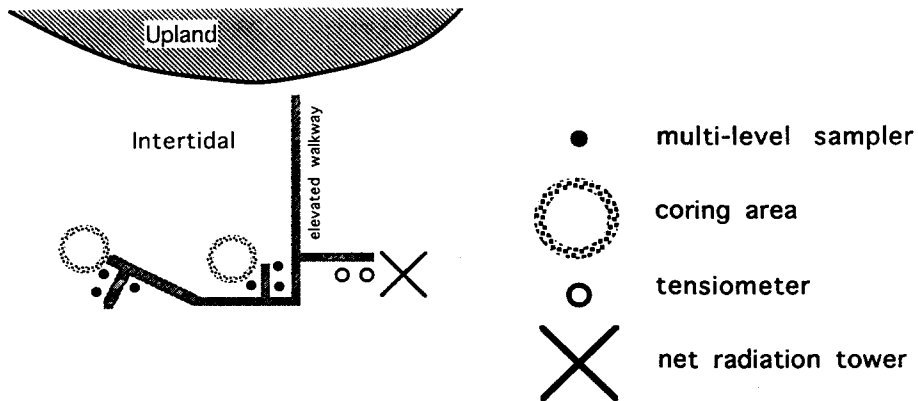
Fig. 2. Detailed map of study site at the Virginia Coast Reserve Long Term Ecological Research site. (See companion paper (Nuttle and Harvey, 1995) for map of general area.)

The sediment surface is inundated by seawater to depth of about 30 cm depending on tidal fluctuations. Inundation generally occurs once or twice daily for an hour or more; between late July and early September in 1989 the fraction of time that the plots were inundated averaged 14.5%. The moisture content of the sediment is maintained at or very near saturation as a result of the periodic inundation with seawater.

3. Methods

3.1. Water balance

Water fluxes across the wetland sediment boundaries were determined in the companion study by Nuttle and Harvey (1995); results are summarized in Fig. 3. The most significant water loss occurred by evapotranspiration (q_E). Water was replaced to the sediment by groundwater inflow from the underlying aquifer (q_V) and by infiltration of seawater when the wetland surface flooded at high tide (q_I); there was no precipitation during the period of study.

Seepage of fresh groundwater across the wetland sediment surface was not quantified by Nuttle and Harvey (1995). Here we summarize the water balance from Nuttle and Harvey (1995) and include an estimate of groundwater seepage to surface water; we assume that groundwater seeps across the sediment surface only when the sediment is fully saturated, i.e. when the wetland surface was flooded at high tide. We estimated the groundwater seepage flux across the surface (q_V^*) by multiplying the total groundwater flux into the wetland sediment, q_V (Nuttle and Harvey, 1995) by the fractional time of tidal inundation of the sediment surface at the study site, α. The flux of groundwater across the sediment surface was small relative to evapotranspiration (Fig. 3).
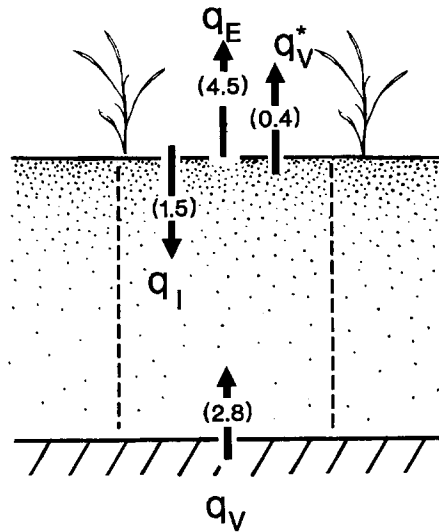
Fig. 3. Water fluxes across wetland sediment boundaries. Fluxes are in millimeters per day; q_E, q_I and q_V are the evapotranspiration, infiltration fluxes, and upward groundwater fluxes, respectively (Nuttle and Harvey, 1995). We also estimated the upward groundwater flux that crossed the sediment surface when the sediment was saturated, q_V^*.

3.2. Macroporosity and effective pore size

Determination of the volume fraction of voids that participates in significant drainage is the most common approach used to estimate sediment macroporosity (Beven and Germann, 1982). Specific yield (S_y), the volume of water drained per unit change in head per unit surface area of sediment, was determined for our sediment by estimating parameters of a water balance model for the system (Nuttle and Harvey, 1994). Macroporosity was calculated from specific yield by dividing S_y by the average porosity determined for the sediment.

The effective diameter of pores at the breakpoint between macropores and matrix pore classes is usually estimated from the capillary pressure equation (Bear, 1972) using measurements of soil water tension at field capacity (Luxmore, 1981). At field capacity rapid drainage through macropores has ceased and further changes in moisture content with time are very slow. At our wetland site the average tension measured at maximum drawdown of the water table during low tide was about 30 cm H_2O. The calculated effective pore diameter for that situation thus estimates the breakpoint pore size which separates macropore from matrix pores.

3.3. Pore-scale variation in solute concentration

Two methods were used to quantify pore-scale variation in chloride concentration: (1) in-situ tension sampling of porewater; (2) homogenization of intact cores. Tension solution samplers work by imposing a pressure gradient in the soil which causes water

to flow toward the sampler reservoir from surrounding pores. Theoretically, the source of porewater to tension sampler reservoirs is expected to be weighted towards the largest wetted pores that contact the sampler intake. The possible range of pore sizes that contribute flow to the sampler is bounded at one end by the largest wetted pores, and at the other end by smaller pores with an effective diameter that depends on the tension applied in the solution sampler. At low applied tensions (less than 100 cm H_2O) the pore-size range of contributing pores is narrow and weighted toward the large pores (Harvey, 1993).

Whole-core homogenization, on the other hand, provides a volume-weighted average for concentration of chloride in porewater. The dominant percentage (95%) of the void volume is the smaller, matrix pores in the sediment; a volume-averaged concentration is therefore representative of the matrix pore concentration.

Porewater samples for determination of chloride concentrations were obtained on three dates—5 August, 9 September and 25 October 1989. Paired sampling at multiple depths was used to determine depth-dependent trends in chloride concentration in each pore-size class. For all samples, chloride concentrations were determined by two-point calibration using an ion-specific electrode. Recalibration was conducted after every sixth sample or when necessary to change concentration ranges. The coefficient of variation for standard determinations repeated throughout the study was 0.04.

Porewater was collected in situ by withdrawal of porewater into reservoirs from six multi-level solution samplers. Multiple reservoirs were housed together in watertight, PVC tubes (5 cm nominal outside diameter) installed vertically into the soil. Reservoirs were located at 2.5, 5.0, 10.0 and 20.0 cm below the sediment surface. Reservoir intakes were covered with porous polyethylene filters which contacted the sediment adjacent to the sampler. Sampling was begun as soon as possible after the wetland surface was exposed following tidal inundation. Each reservoir was evacuated and suction was applied (100 cm H_2O); suction was maintained by closing stopcocks connected to the Tygon tubing that ran to the surface. Thirty minutes later porewater was withdrawn from reservoirs through the Tygon tubing using the suction created with a sampling syringe. A second Tygon tube to each reservoir was used to relieve the build-up of suction, and to clear the reservoir and tubing of sample. Between sampling, a nitrogen atmosphere was maintained in each reservoir by flushing Tygon tubes under pressure from a portable tank. Porewater samples were also withdrawn directly from conspicuous macropores using a syringe inserted to a depth of 1 cm.

Four intact cores (5 cm diameter) were obtained using a thin-walled, aluminum coring barrel. Teeth were filed and highly sharpened on the cutting edge of the core barrel to minimize compression or disturbance around roots. Cores were extruded immediately onto a flat work surface, sliced into 1 cm increments, and sealed in plastic bags for transport to the laboratory. Core samples were weighed, diluted with measured amounts of deionized water, homogenized, and allowed to stand overnight. Sample aliquots (5 ml) were removed for determination of chloride concentration. Overnight storage of the initial sample set was repeated for an additional night in a shaker bath. Final results were unaffected by additional storage so that use

of the shaker bath was discontinued. The remaining homogenized samples were oven dried at 100°C and reweighed. Oven temperature was not a factor in weight-loss determination, as indicated by a test where samples were freeze-dried and weighed prior to oven drying. Final chloride concentrations were adjusted by accounting for the dilution of initial water volume by the volume of added deionized water.

3.4. Model for chloride transport in matrix pores

Our hypothesis specifies that upward advective transport occurs in matrix pores, which implies that, if salt becomes concentrated beneath the surface as a result of evapotranspiration, both an upward and downward diffusive flux of salt will occur away from the depth of maximum concentration. The governing equation for transport is

$$D_L \frac{\partial^2 c}{\partial z^2} - v \frac{\partial c}{\partial z} = \frac{\partial c}{\partial t} \tag{1}$$

where c is concentration, D_L is a vertical dispersion coefficient, v is a vertical pore-water velocity, and z is the vertical distance coordinate which equals zero at the sediment surface and increases into the sediment. For present purposes, we assume steady-state conditions, i.e. $\partial c / \partial t = 0$. The boundary conditions for the model are

$$c(0) = c_s$$
$$c(\infty) = c_b \tag{2}$$

where c_s and c_b are measured chloride concentrations in matrix pores at the sediment surface and at depth, respectively. The solution for (1) subject to the boundary conditions is

$$c(z) = c_b + (c_s - c_b) \exp(-zv/D_L) \tag{3}$$

The upward porewater velocity, v, was set equal to the evapotranspiration flux of Nuttle and Harvey (1995) divided by the porosity. The model was then fitted to observed chloride concentration data by adjusting the dispersion coefficient.

3.5. Sediment chloride budget

A general expression for the mass balance of chloride in the sediment is

$$\Delta_S = J_i - J_o \tag{4}$$

where Δ_S is the rate of change in storage of chloride in sediment porewater, and J_i and J_o are the rates of input and output of chloride to and from the sediment, respectively. In this paper we do not explicitly consider chloride transport by plant root uptake and secretion from leaves or bioturbation in the chloride balance. Instead, we test to see whether the upward diffusive efflux of chloride and the advective export of chloride owing to the upward flux of groundwater from below the wetland are sufficient to balance the input of salt and the change in storage. The mass balance for the stated

conditions is

$$\Delta_S = q_I c_s - \alpha\phi D_s \frac{\partial c}{\partial z}\Big|_{z=0} - q_V{}^* c\big|_{z=0} \tag{5}$$

where q_I is the infiltration water flux, c_s is the average chloride concentration in overlying surface water, D_s is the diffusion coefficient for chloride in this sediment, α is the fraction of time that the wetland surface is inundated with surface water, and $q_V{}^*$ is the rate of groundwater seepage across the wetland surface (Fig. 3). We argue that if the conceptual model is correct then the second term on the right-hand side of Eq. (5) will be large enough to balance chloride input to the sediment by infiltration and change in storage in porewater. Our expectation was that the advective flux of chloride across the surface owing to upward groundwater transport (the third term on the right-hand side of Eq. (5)) would be negligible during late summer when potential evaporation is high.

The chloride budget was determined for the period 5 August–9 September. Change in storage of chloride in porewater was computed using chloride concentration profiles determined by coring on 5 August and 9 September and the sediment porosity. The infiltration flux q_I and the vertical groundwater flux $q_V{}^*$ are from Nuttle and Harvey (1995) and from Fig. 3, respectively. The fractional time of sediment inundation, α, was determined from a record of tide stage made between 5 August and 9 September. The change in chloride storage in the sediment porewater was estimated from data collected on 5 August and 9 September. Soil porosity was measured by gravimetric methods. The diffusion coefficient, D_s, was estimated for this sediment following Archie's Law (Berner, 1980) using

$$D_s = \frac{D_0}{F} \tag{6}$$

where D_0 is the diffusion coefficient for chloride in seawater at 25°C (Li and Gregory, 1974), and F is a formation factor that was approximated by ϕ^{-2}. The estimated diffusion coefficient for chloride in this sediment is 3.3×10^{-6} cm^2 s^{-1}. The procedure to estimate the upward concentration gradient, $\delta c/\delta z$, is explained in Section 4.4.

4. Results

4.1. Macroporosity

Macropores accounted for about 5% of the pore volume and matrix pores for 95%. The breakpoint effective pore diameter separating macropores and matrix pores was 100 μm, which is consistent with a number of classifications separating macropores from smaller pores (Beven and Germann, 1982; Luxmore et al., 1990).

4.2. Chloride concentrations from in situ tension samplers vs. homogenized cores

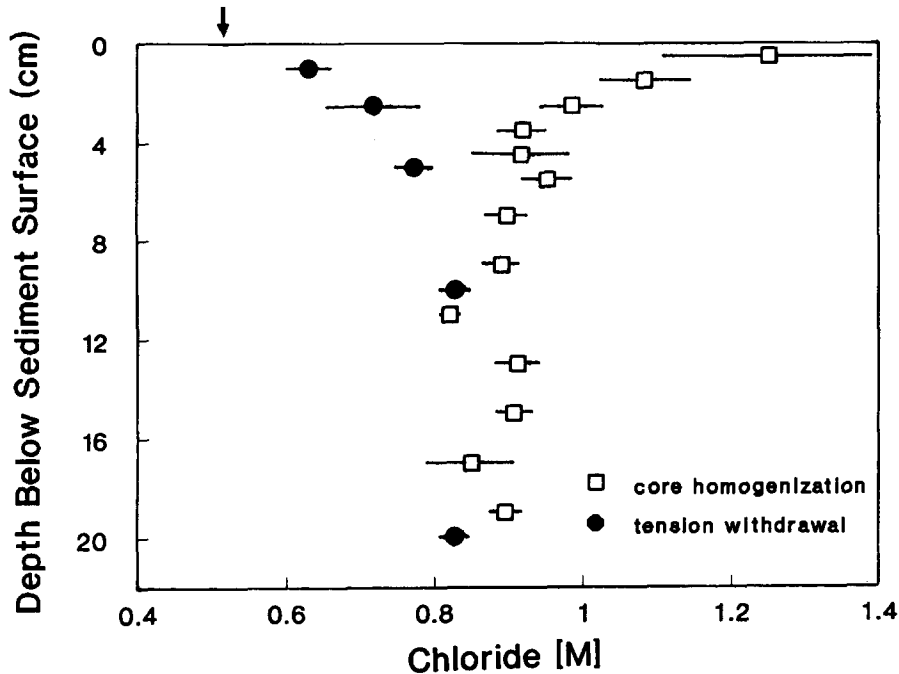Chloride concentrations were consistently lower in porewater extracted with in situ

Fig. 4. Chloride concentrations plotted vs. depth in sediment on 5 August 1989. Mean values represent four replicates per depth for homogenized cores and six replicates per depth for in situ tension sampling. Error bars are standard errors. Vertical arrow indicates chloride concentration in surface water.

tension samplers vs. homogenized cores from the same depths (Fig. 4). The greatest difference in concentration provided by the two methods was at the shallowest paired sampling depth (2.5 cm), where homogenized concentrations exceeded tension sampler values by twofold or more. The concentration differences declined with depth until indistinguishable below 10 cm. This pattern was observed for all three sampling dates.

4.3. Observed vs. modeled chloride depth distribution

The highest observed concentration of chloride was in matrix pores, and concentrations in the matrix pores declined exponentially with depth, in accordance with theoretical expectations. A model for upward flow in matrix pores carrying chloride toward the wetland surface in opposition to a downward diffusive flux of chloride described observed chloride data from homogenized cores reasonably well (Fig. 5). A vertical advective velocity for the model was estimated by dividing the evapotranspiration flux by the porosity determined in the present study (0.42). The observed vertical distribution of chloride in matrix pores was closely fitted by the model by adjusting the only free parameter in the model, the dispersion coefficient. By fitting we estimate an average vertical dispersion coefficient to be 7.5×10^{-6} cm s^{-1}.
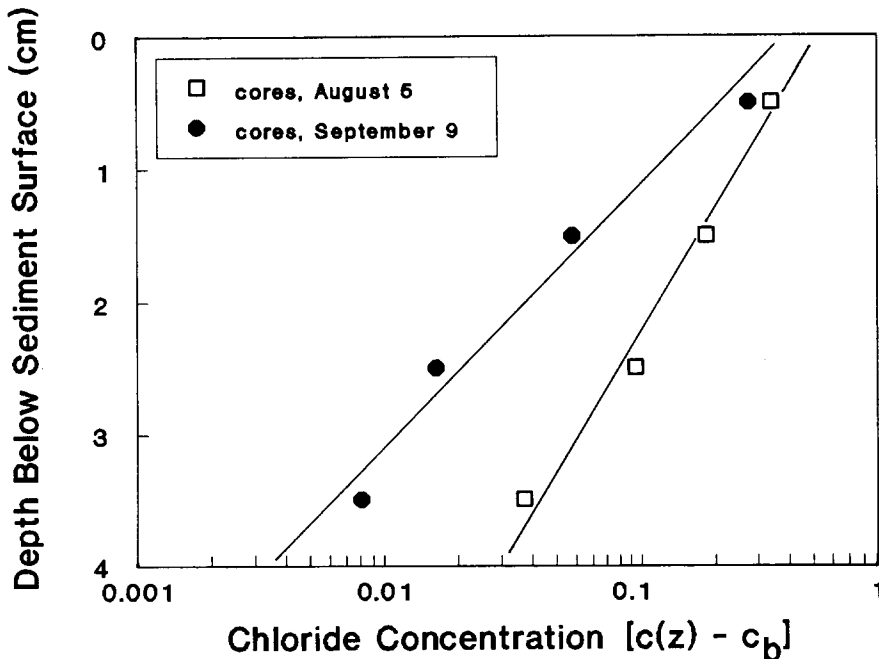
Fig. 5. Chloride concentration in matrix pores (determined by core homogenization) vs. depth below sediment surface. The field-measured depth distributions for chloride are closely approximated by linear fits on the semi-log plot. The linear fit is implied by the exponential form of the transport model in Eq. (3).

4.4. Does chloride diffusion from matrix pores to surface water balance input by infiltration?

High chloride concentrations in matrix pores just beneath the sediment surface imply high rates of diffusion into surface water when the sediment is inundated. We address whether a diffusive export of chloride to surface water is sufficient to balance the advective input by estimating and comparing magnitudes of the components of the chloride balance in (5).

Chloride influx to the wetland sediment averaged 0.085 mmol cm^{-2} day^{-1} during the study period and 0.059 mmol cm^{-2} day^{-1} was removed from storage. A total export flux of 0.144 mmol Cl cm^{-2} day^{-1} is required to balance chloride input by infiltration and release from storage. To calculate the diffusive export term in (5), the upward concentration gradient near the sediment surface had to be estimated. A two-point linear fit to the concentration gradient utilizes the top chloride measurement in the sediment and the surface water concentration only. This approach ignores the trend of increasing concentration toward the surface and is expected to underestimate the export flux. A second approach which is commonly employed is to use an exponential curve fit to extrapolate concentrations toward the surface (Callender and Hammond, 1982).

Here we used the second approach to calculate the upward concentration gradient.
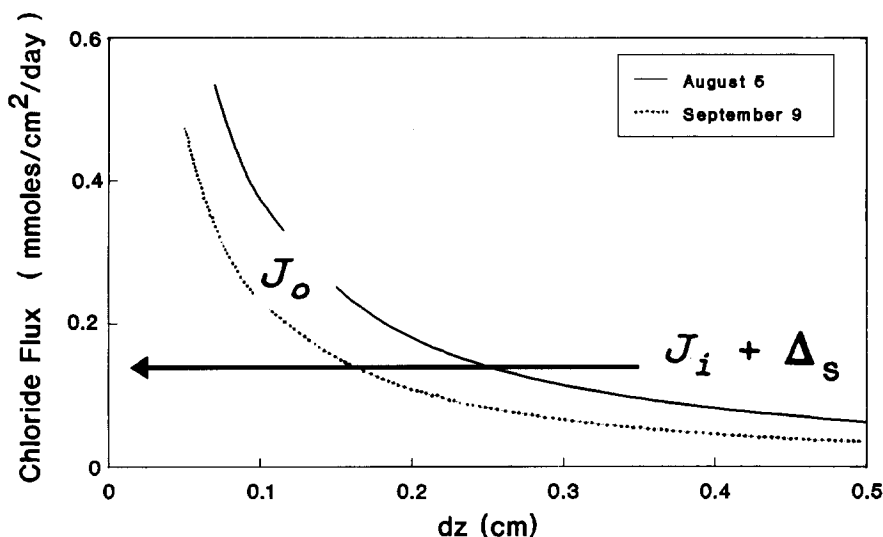
Fig. 6. Computed upward diffusive chloride flux from matrix porewater to surface water (J_o) vs. dz, the depth interval used to determine the chloride concentration gradient at the sediment surface. The concentration gradient was estimated by extrapolating the concentration trends shown in Fig. 5 toward the sediment surface. For comparison, the horizontal arrow labeled $J_i + \Delta_S$ indicates the sum of the chloride infiltration rate and the rate of change in chloride storage. Those fluxes are balanced by a diffusive efflux of chloride from matrix pores if the concentration trends are extrapolated to approximately 0.2 cm below the sediment surface.

Matrix chloride concentrations were extrapolated towards the sediment surface using the exponential relationships shown in Fig. 5. An upward concentration gradient and diffusive efflux were then computed for a series of extrapolated concentrations above 0.5 cm. If the measured trend of increasing chloride concentrations toward the surface is extrapolated to approximately 0.2 cm below the surface then diffusive export from matrix pores is sufficient to balance the rate of chloride input to the sediment by infiltration and the change in chloride storage in the sediment (Fig. 6). The extrapolated concentrations at 0.2 cm below the sediment surface, 1.37 mol l^{-1} and 1.06 mol l^{-1} of chloride, respectively, are equivalent to less than 100 parts per thousand of salinity. Those extrapolated concentrations are not unreasonably high given that they are below saturation for chloride salts (Drever, 1982), and given that salinities of up to 200 parts per thousand have been previously measured in coastal wetlands (Casey and Lasaga, 1987).

4.5. Flushing of chloride by groundwater discharge

In the expansive interior areas of coastal wetlands vertical discharge of groundwater out of the sediment could potentially flush some salt from the sediment (Nuttle and Harvey, 1995). At our site the groundwater seepage flux across the wetland surface was less than 10% of the evapotranspiration flux at our site (Fig. 3). We estimate that flushing of chloride by groundwater seepage equals 0.04 mmol cm^2

day^{-1}, or less than 30% of the measured chloride input and change in storage in the sediment. Salt flushing might be important during cooler parts of the year when evapotranspiration is lower. The potential widespread importance of groundwater seepage as a mechanism of reducing sediment salinity remains unknown, partly because groundwater inflow has rarely been estimated in hydrological studies of coastal wetlands (Harvey and Odum, 1990).

5. Discussion

5.1. Pore-scale segregation of infiltration and evaporation-driven fluxes

We found that chloride was highly concentrated in matrix cores but relatively dilute, similar to seawater concentrations, in macropores. Chloride concentrations would not be expected to differ significantly between pore sizes if infiltration and evaporation fluxes occur uniformly across the sediment surface regardless of pore size. Our findings suggest that infiltration occurs preferentially through macropores. Previous studies in coastal wetlands support this interpretation. Casey et al. (1986) noted rapid movement of ^{7}Be to a depth of 8 cm in a single infiltration event in a salt marsh soil. Hemond and Chen (1990) and Harvey (1993) found highest concentrations of surface applied solute tracers in the network of largest pores.

Small pores of the matrix are the dominant fraction of pore space (95%) and the principal reservoir for porewater storage in the sediment. Using chloride as an environmental tracer, we tested whether evaporation occurs principally from matrix pores. Large differences in solute concentration exist between matrix pores and macropores at all depths above 10 cm (Fig. 4); those concentration differences must be maintained by pathways of water movement or otherwise the concentration gradient would be eliminated over time by diffusion. A net water flux from macropores to the matrix could maintain the observed concentration differences in pore-size networks. Our interpretation is that upward advection occurs principally from the matrix to satisfy the atmospheric demand for water imposed by evaporation at the sediment surface. Desaturation occurs in the sediment by the withdrawal of macropore water into the surrounding matrix.

Field observations suggest that downward infiltration has only a minimal effect on chloride concentrations in the matrix pores. Observed chloride concentrations in matrix pores were much higher than seawater chloride concentrations and they were highest at the sediment surface. A model for upward flow in matrix pores in Eq. (3) provided a close match to measured chloride concentrations in matrix pores (Fig. 5), providing further support for the conceptual model. The fitted dispersion parameter from (3) has a physically reasonable value, being about two-fold higher than the coefficient of molecular diffusion for chloride in this sediment estimated using the measured porosity and data from Li and Gregory (1974). Further quantitative support came from constructing a rough solute budget which demonstrated that, using reasonable assumptions in estimating the concentration gradient across the sediment surface under flooded conditions, the rate of chloride diffusive efflux was

sufficient to balance the estimated rate of chloride input by infiltration and the measured change in chloride storage in sediment. Field observations and modeling evidence therefore both supported the interpretation that infiltration and evaporation fluxes were segregated by pore size.

5.2. Effect of pore-scale segregation on sediment salinity

We found that the interaction of subsurface advection and diffusion with sediment macroporosity had significant effects on solute cycling in coastal wetlands. The accumulation of chloride at high concentrations in matrix pores at the soil surface increased the diffusive flux of chloride from the sediment to surface water when the wetland was flooded. Enhanced export of chloride was facilitated by segregation of water fluxes; without macropores a higher inventory of chloride at depth would be required to achieve the same diffusive efflux to surface water because salt would be continually flushed downward by infiltrating seawater. The interaction of soil structure, advection and sediment macroporosity may therefore be important to maintaining lower average soil salinities. Cycling of other solutes between wetland sediment and estuarine surface water, including dissolved nutrients, metals and radionuclides, is likely to be affected as well.

5.3. Implications for solute sampling in wetland sediments

The tension solution sampling method did not detect the steep diffusive concentration gradient from matrix pores to surface water, because of preferential sampling of macropore water. Differences in chloride concentration in macropores and matrix pores were most pronounced near the sediment surface (Fig. 4). Chloride concentrations in macropores were only slightly higher than surface water concentrations, in contrast to matrix pore concentrations which were twofold higher compared to surface water. Our study therefore suggests that diffusive fluxes from coastal wetland sediments will be underestimated if the tension solution sampling method is used to determine the concentration gradient. For chloride, the more appropriate technique to determine matrix concentrations is whole-core homogenization. Upward advection in matrix pores concentrates solutes just below the surface and increases the need for closely spaced sampling, to estimate accurately the solute concentration gradient in diffusive calculations.

6. Summary

The interaction between macropores, subsurface advection, and diffusion was examined in a coastal wetland sediment, and effects on chloride transport were quantified. We found that recharge and discharge fluxes were partitioned between macropores and matrix pores, respectively. At high tide, surface water preferentially infiltrated macropores, which kept chloride concentrations in macropore water relatively similar to that of seawater. At low tide, water loss from the sediment

occurred by uptake of macropore water into the matrix and evaporation from matrix pores. Matrix water had much higher chloride concentrations owing to evapoconcentration.

Segregated fluxes in pore-size networks therefore create and maintain a micro-scale chemical–porewater environment of extreme importance within millimeters of the sediment surface. The upward delivery of chloride in matrix pores had the effect of augmenting diffusion, by maintaining a concentration of chloride much higher than that of seawater in porewater just below the sediment surface. When the wetland flooded, segregation of matrix pores from infiltration fluxes allowed upward diffusion from matrix pores to surface water to occur without disruption by downward infiltration in macropores. Understanding controls on chloride flux and concentration in coastal wetlands has direct bearing on primary productivity, and on biogeochemical cycling and material and energy exchanges between the wetlands and adjacent estuarine and coastal waters. We believe that advection-augmented diffusion from matrix pores to surface water is an important regulator of the salt balance of coastal wetland sediments, which could affect productivity of the dominant vegetation. For example, evaporation-augmented diffusion from matrix pores to surface water could be important in maintaining sublethal concentrations of chloride for the highly productive vegetation in coastal wetlands. Cycling of other solutes, including dissolved nutrients and metals, is undoubtedly affected as well. Characterization of reactive solute transport across the sediment surface requires further development of innovative techniques to sample at such fine scales.

Acknowledgments

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