Peat porewater chloride concentration profiles in the Everglades during wet/dry cycles from January 1996 to June 1998: field measurements and theoretical analysis[†]

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Abstract:

Water quality is a key aspect of the Everglades Restoration Project, the largest water reclamation and ecosystem management project proposed in the United States. Movement of nutrients and contaminants to and from Everglades peat porewater could have important consequences for Everglades water quality and ecosystem restoration activities. In a study of Everglades porewater, we observed complex, seasonally variable peat porewater chloride concentration profiles at several locations. Analyses and interpretation of these changing peat porewater chloride concentration profiles identifies processes controlling conservative solute movement at the peat–surface water interface, that is, solutes whose transport is minimally affected by chemical and biological reactions. We examine, with an advection–diffusion model, how alternating wet and dry climatic conditions in the Florida Everglades mediate movement of chloride between peat porewater and marsh surface water. Changing surface water–chloride concentrations alter gradients at the interface between peat and overlying water and hence alter chloride flux across that interface. Surface water chloride concentrations at two frequently monitored sites vary with marsh water depth, and a transfer function was developed to describe daily marsh surface water chloride concentration as a function of marsh water depth. Model results demonstrate that porewater chloride concentrations are driven by changing surface water chloride concentrations, and a sensitivity analysis suggests that inclusion of advective transport in the model improves the agreement between the calculated and the observed chloride concentration profiles. Copyright © 2007 John Wiley & Sons, Ltd.

INTRODUCTION

Everglades water quality is a focal point of the largest water reclamation and ecosystem management project proposed in the United States and possibly the world (*The Everglades Restoration Project*, Associated Press, 14 October 2004). *Public Works* (October 2006, page 42) termed the Comprehensive Everglades Restoration Plan (CERP) "the largest ecosystem restoration effort in the world". A quantitative understanding of water and solute exchange (Krest and Harvey, 2003; Harvey *et al.*, 2004) between surface water and peat porewater is essential for successful Everglades restoration (Gough *et al.*, 2000; Snodgrass *et al.*, 2000).

Peat formation, accumulation and destruction are important processes in the Everglades ecosystem. Reduced microbial metabolism and plant decomposition in the Everglades lead to organic matter accumulation and peat

formation in the 1600 ha South Florida Water Management District Water Conservation Area 2A (WCA-2A) (Figure 1), which was impounded in the early 1960s by a series of levees and canals. The WCA-2A is bounded on the north by the Hillsboro Canal and is located southeast of the Everglades Agricultural Area (EAA). Impoundment changed (lengthened) the Everglades hydroperiods (the duration and frequency of flooding of the Everglades) and this resulted in an increase in the rate of organic soil accretion in northern WCA-2A by a factor of 3–5 (Craft and Richardson, 1998). In parts of WCA-2A peat is more than 1 m thick (Davis and Ogden, 1994) (Figure 2). Peat mercury, phosphorus and sulphur, for example, have been implicated in Everglades' water quality and ecosystem health issues (Koch and Reddy, 1992; Craft and Richardson, 1998; Snodgrass, 2000). Metals, nutrients and contaminants accumulated in Everglades' peat over time are mobilized in peat porewater and exchange with overlying Everglades surface water by advection and diffusion. Transport of chemical constituents from peat porewater could have important consequences for Everglades ecosystem restoration activities. Exchange of both water and solutes occurs in either direction

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at the peat–surface water interface depending on the time-varying direction of the water flux and the time-varying peat porewater–surface water interfacial gradient in solute concentration.

Physical, chemical and/or biological processes regulate chemical transport at the peat–surface water interface (Meyers *et al*., 1993; Romanowicz *et al*., 1994). Also, groundwater recharge and discharge may modify transport to and from peat (Harvey *et al*., 2004). As a first step to better understanding of rates and processes involved in the mobilization and transport of non-conservative constituents (e.g. certain metal species, nutrients and contaminants) in the Everglades ecosystem, scientists must identify and quantify physical processes that govern transport of conservative constituents across the peat interface so that resource managers can make sound decisions concerning peat contributions to overlying water. We feel that a process-based quantitative analysis of peat porewater chloride concentration profiles will help identify key physical processes controlling the transport of conservative constituents across the peat–surface water interface in the Everglades and elsewhere.

During a long-term, intensive study of Everglades' water quality (during the late 1990s), we observed complex, seasonally variable chloride concentration profiles in peat porewater at several locations. Our interpretation of these observed peat porewater chloride concentration profiles assumes that varying Everglades water levels, termed hydroperiods, modify Everglades surface water chloride concentrations, and thereby influence chloride transport to and from peat by altering the magnitude and direction of the driving force for diffusion, i.e. the chloride concentration gradient. This change in the benthic flux of a solute in response to perturbations in overlying water concentrations has been demonstrated for the

biologically active solute, zinc (Kuwabara *et al*., 2003). Dilution by rainfall and evapoconcentration of chloride by evaporative/transpiration (ET) processes modify the chloride concentration and we assume that the magnitude of this water volume change is correlated to an available surrogate variable (water level). We also hypothesize that peat porewater chloride concentration profiles can also be modified by advection into or from peat in response to varying marsh water levels, and that local effects in the peat such as evapoconcentration near root surfaces and the presence of root casts have a negligible impact on the peat porewater chloride concentration profiles.

To test the hypothesis that changing surface water volume and depth associated with changing hydroperiods modify solute flux from peat, we quantitatively analysed data for surface water and peat porewater chloride concentrations at two Everglades research sites and water level data at a third site, on three dates, during 1996–1998. Since chloride is hydrologically considered a conservative constituent, modelling of chloride transport into and out of peat porewater allows analysis of the mechanisms of advection and diffusion in the absence of any other chemical reactions or biological processes.

Everglades water levels were characterized in this paper using water depth data from three research sites in the northern part of WCA-2A. Surface water and peat porewater chloride concentrations are used with an advection–diffusion model to evaluate contributions of advection and diffusion to mass transport of chloride in peat. Although models similar to ours have been used to describe concentrations of chloride in peat porewater at other locations, the application of this model to the Everglades is novel because of the variations over event-specific to seasonal timescales of chloride concentrations in surface water. The approach for characterizing chloride concentrations in peat porewater (1) has general applicability for characterizing the influence of time-varying surface water levels in wetlands, on potential benthic fluxes of conservative solutes in the Everglades and other organic-rich wetlands, and (2) provides a physical basis for developing process-integrated models describing the benthic flux of non-conservative solutes.
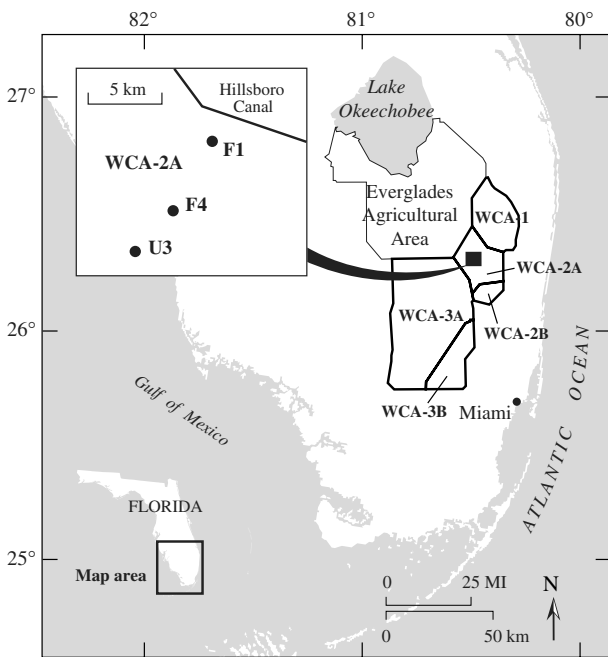
SITE DESCRIPTION

This report presents data for three research locations in WCA-2A, sites F1 (26°21′35″N, 80°22′14″W), F4

Figure 1. Map showing the extent of Water Conservation Areas (WCA) and the location of three monitoring sites within WCA-2A (inset)
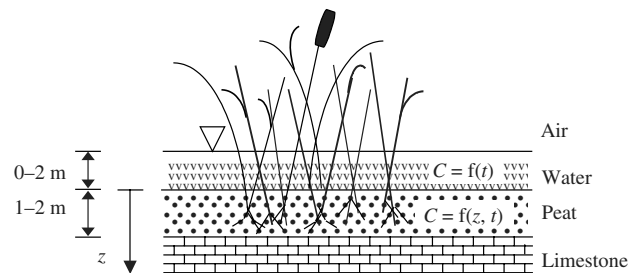

Figure 2. Schematic diagram of a marsh cross-section showing peat accumulation on limestone in the Everglades

(26°19′00″ N, 80°23′07″ W) and U3 (26°17′15″ N, 80°24′41″ W) (Figure 1) within a continuous, constructed wetland complex, surrounded by levees and water supply canals. Site F1, a eutrophic site with luxuriant cattail growth within the northern segment of WCA-2A, periodically receives nutrient-enriched canal water (originating in the EAA) from the Hillsboro Canal (Figure 1). Water quality in WCA-2A is increasingly oligotrophic moving southward from site F1 (Koch and Reddy, 1992) because of the influence of nutrient uptake and mixing of nutrient-rich canal water inputs with rainfall and marsh water (McCormick *et al.*, 1996). Site U3, located about 5 miles south of site F1 in an oligotrophic part of WCA-2A, is away from Hillsboro Canal water inputs and has less dense, predominantly sawgrass vegetation. Site F4, located approximately midway between sites F1 and U3, is also away from canal water inputs and has less dense, predominantly sawgrass vegetation than at site F1. Daily stage data available at site F4 was needed to develop a transfer function relating chloride concentration at site U3 to stage at site F4.

Usually, summers are wet and winters are dry in the Everglades. Frequent wet periods from May to October are characteristic of WCA-2A; other months are generally dry with occasional rainstorms (Meyers *et al.*, 1993). The climate of southeast Florida is characterized by a warm dry season (November to April) and a humid, wet season (May to October). Annual precipitation averages 50–62 inches in this area with between 65–80% falling between May–September due to a nearly daily pattern of thunderstorms (USGS, 2005). Peat at WCA-2A is typically covered by up to a metre of water, but during intermittent dry periods water levels drop (sometimes > 50 cm) and peat surfaces approach desiccation. Everglades peat porewater is often strongly reducing because of high organic carbon concentrations (for example, at site F1 the mean of 18 dissolved organic carbon in water measurements during the period of study was 114 mg C litre^{-1} and for site U3 the mean of 19 measurements was 55 mg C litre^{-1} during the same interval) and intensive microbial processes.

MATERIALS AND METHODS

Water level data and samples for chemical analysis at sites F1, F4 and U3 were obtained on different schedules and at different frequencies (Table I). Daily water levels at site F4 were measured by the US Geological Survey (USGS) Florida Water Science Centre (German, personal communication, 2001) with a float-driven potentiometer sensor (German, 2000). Daily stage data at site F4 is used to develop a transfer function for the model's time-varying surface water chloride concentration boundary condition at sites F1 and U3. At sites F1 and U3, monthly stage measurements were determined by the South Florida Water Management District by visual inspections of staff gauges.

Surface waters were sampled and analysed monthly at sites F1 and U3 for chloride concentrations by the

Table I. Data availability for the WCA-2A sites F1, F4 and U3 between 4 January 1996 and 19 May 1998

Data	Site F1	Site F4	Site U3
Stage measurements	Monthly	Daily	Monthly
Chloride concentrations in surface water	Periodically	Monthly	Monthly
Chloride concentrations in porewater	Periodically	Not available	Periodically

South Florida Water Management District, using standard US Environmental Protection Agency (USEPA) methods (McCormick *et al.*, 1996). Some monthly measurements of surface water chloride concentration are not available because sampling sites were inaccessible due to low water levels. Additional information concerning onsite and laboratory procedures are available in Reddy and Aiken (2001) and references therein.

Peat porewater samples were obtained using a closed-interval, low-volume, stainless steel USGS minipoint sampler system (Duff *et al.*, 1998). This in situ sampling system minimized porewater mixing during sampling and allowed well-defined sampling intervals (5–100 cm) below the peat surface. A transparent manifold served as an interface reference surface. Replicate peat porewater sampling demonstrated acceptable porewater concentration reproducibility. For duplicate and replicate samples collected at site U3 during June 1996 the average deviation between replicate samples at 5 cm and at 20 cm, and replicate samples at 30 cm depth taken from the left and right side of the sampling platform, was <1% (Schuster, 2005, unpublished results). The USGS minipoint sampler allowed sampling of peat porewater in a reliable and reproducible way that, because of the high water content of the peat, was not possible using conventional core extrusion methods. Dialysis samplers were considered but not used because they require long equilibration times and could not capture the short-term variation in peat porewater concentrations.

Chemical analyses of peat porewater and surface water samples obtained by USGS scientists were done at the USGS research laboratories in Boulder, Colorado. Samples for chloride determination were filtered (0·45 μm pore size) onsite and refrigerated until analysis by automatic titration of chloride (Cotlove *et al.*, 1958). Quality control and quality assurance procedures included analyses of blanks and standard water reference samples. Chloride analyses performed routinely on these reference samples were within accepted limits. The average percent difference of observed versus expected chloride values for three USGS Standard Water Reference Samples certified for chloride content (analysed between May 1996 and April 1997) was <1%.

Measurements of stage and chloride concentrations

Stage measurements. During the period January 1996 to June 1998, water depths at sites F1, F4 and U3 varied significantly. For example, measured water depth

at site F4 ranged from a low of about 0·1 m below the peat surface in April 1997 to a high of 0·8 m above the peat surface in March 1998 (Figure 3a). Surface water volume reductions during dry periods cause a concomitant increase in surface water chloride concentrations (Figure 3b). That is, during dry periods, high evaporation, little or no rainfall and minimum canal water inputs lead to decreased water levels and increased salinity in WCA-2A.

Monthly water depth measurements at site U3 were the same as the coincident daily water depth measurements at site F4 during this interval, except for data for 18 September 1997 when the depth values differed by 0·01 ft (Figure 3a). Monthly water depth measurements at site F1 correlated less well with coincident water depth measurements at site F4 ($r^2 = 0.45$, n = 11, significant at the 0·01 level). Water depth measurements at site F1 were higher than at sites F4 and U3, in some cases by as much as 0·4 m (summer of 1997) (Figure 3a).

During Everglades dry periods (November–May) daily evaporation consistently exceeds daily rainfall (German, 2000) resulting in low water levels (water depth approaching 0 m) and, on occasion, peat desiccation (a nearly complete drying-out of water not chemically bound) and the loss of water from pore spaces of peat soils as a result of direct evaporation.

Surface water and peat porewater samples collected in June 1996 are representative of water quality during a contemporary wet period; water levels were near the highest observed during this study with no reports of peat dessication (Figure 3a). In June 1996 water depths at site F4 were about 0·6 m. Water depths were at this level in October 1996, June 1997 and December 1997. In March 1998 water levels at site F4 were about 0·8 m. Minimum water depths in WCA-2A occurred during April 1997

and samples obtained at this time represent surface water quality during the driest conditions of this study.

Surface water chloride concentrations. Surface water chloride concentrations were generally lower at sites F1 and U3 in wet hydroperiods than in dry hydroperiods (Figure 3b). For example, mean surface water chloride concentrations at site F1 for samples obtained during the dry period (November–April, n = 9) were significantly different than the mean surface water chloride concentration for samples obtained during the wet period (May–October, n = 6) for the period 30 December 1996 to 21 April 1998. For the dry period at site F1 the mean (±98% confidence level) was 280 mg Cl litre^{-1} (±58 mg Cl litre^{-1}) while for the wet period at the same site the mean (±98% confidence level) was 138 mg Cl litre^{-1} (±40 mg Cl litre^{-1}). The 98% confidence levels for the mean wet and dry chloride concentrations do not overlap. The mean surface water chloride concentration differences between dry and wet periods were also statistically different at the U3 site (at the 90% confidence level over the period 4 January 1996 to 19 May 1998). Samples collected during the dry period at site U3 had a mean value (±90% confidence level) of 168 mg Cl litre^{-1} (±21 mg Cl litre^{-1}) while for the wet period the mean (±90% confidence level) was 128 mg Cl litre^{-1} (±17 mg Cl litre^{-1}). The mean surface water chloride concentration values at site U3 (with the 90% confidence intervals) collected during the wet and the dry periods do not overlap.

Peat porewater chloride concentrations. Peat porewater chloride concentrations, at as many as seven depths and down to 165 cm into the peat, were measured at sites F1 and U3 for selected sampling times (Figure 4). Chloride concentrations near the peat–surface water interface show a linear gradient within the top 10–20 cm of peat indicating little peat porewater–surface water mixing at
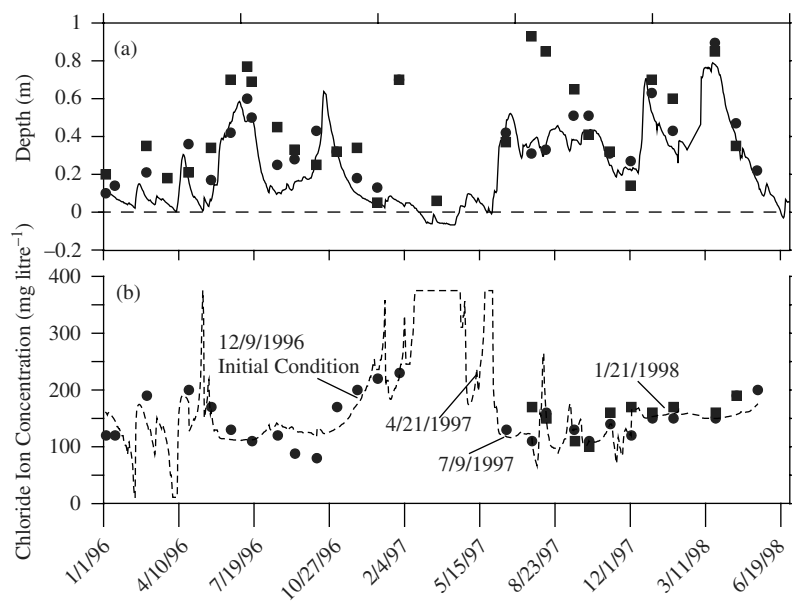

Figure 3. (a) Daily stage measurements at site F4 (solid line) and monthly stage measurements at sites U3 (●) and F1 (■). (b) Chloride surface water concentrations at sites U3 (●) and F1 (■) as functions of time. The dashed curve was calculated using the surface water chloride concentration at site U3 versus (inverse) water depth correlation in Table II
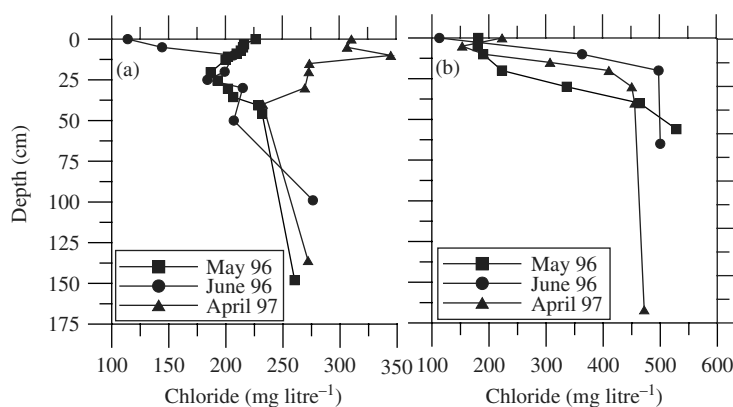
Figure 4. Chloride concentrations in peat porewater as a function of depth into the peat at three dates for sites (a) U3 and (b) F1 in WCA-2A. In this plot, lines connect data points

the peat–surface water interface. If there was complete mixing near the interface, there would be a constant value of chloride concentration from the peat–surface water interface into the peat. Otherwise, advection–diffusion gives a curved profile. Porewater mixing could be due to bioturbation, wave action or other turbulent interfacial mixing processes. Vegetation at and near the F1 and U3 sampling sites may serve to minimize wind- and wave-induced mixing at the peat–surface water interface. Absence of wind-induced mixing has also been reported at other locations (Dauwe *et al.*, 1999).

With the exception of April 1997 at site U3, peat porewater chloride concentrations had maximum measured values below 60 cm depth. For example, at site U3, on three different dates, the concentration at the deepest sample was about 275 mg litre^{-1}, despite significant fluctuations in peat porewater concentrations close to the surface. At sites F1 and U3, these limit values were about 275 mg litre^{-1} and 500 mg litre^{-1}, respectively. Chloride concentrations deep in the peat at site U3 are similar to values reported by Meyers *et al.* (1993), at the southern edge of WCA-3A (to the south of WCA-2A), which had chloride concentrations in the range of 250 to >280 mg litre^{-1}. At site U3, in May and June of 1996, surface water chloride concentrations were lower than concentrations deep in the peat, but in April 1997 the opposite was observed (Figure 4). At site F1, surface water chloride concentrations were less than concentrations deep in the peat, for all three sampling dates (Figure 4).

PEAT POREWATER CHLORIDE CONCENTRATION MODEL DEVELOPMENT

An advection–diffusion model was developed to describe the mass transport of chloride in the WCA-2A peat porewater. As a conservative tracer, no sorption or other chemical reactions are assumed to affect chloride mass. Landva and Pheeney (1980), in considering mass transport to and from peat, noted that total peat porosity can exceed 90%. Average peat porosity at sites F1 and U3 (0.93 ± 0.028 and 0.93 ± 0.034, respectively (mean ± one standard deviation)) is the same (Gilmour *et al.*,

1998) and, for simplicity, peat is considered to be a uniform medium with a porosity of 1 (i.e. there is little mineral matrix phase, only liquid water).

Advection of peat porewater to and from the peat may influence the chloride peat porewater concentration profile. Cornett *et al.* (1989) have shown that small interstitial velocities can impact observed peat porewater concentration profiles, and Meyers *et al.* (1993) have given geochemical evidence of groundwater movement in the unconfined Everglades surficial aquifer. Although estimated average interstitial velocities in WCA-2A are low (0·06 cm day^{-1} out of the peat into the overlying surface water at U3 and 0·17 cm day^{-1} out of the peat into the overlying surface water at F1) (Harvey *et al.*, 2002), the potential for chemical flux due to advection may be significant (Ours *et al.*, 1997), and thus advection was included in the model.

The Peclet number *Pe* is a dimensionless group that expresses the ratio of advective transport to diffusive transport. At the pore scale, it can be defined as:

$$Pe = \frac{|u|L}{D_{eff}} \tag{1}$$

where L is a characteristic length (m) (mean grain diameter or pore diameter) of the porous medium and $|u|$ is the magnitude of the interstitial velocity (de Marsily, 1986). Assuming a 1 mm effective pore diameter in the peat, the average interstitial velocity reported by Harvey *et al.* (2002) at site F1 of 0·17 cm day^{-1} and a D_{eff} (the effective diffusion coefficient for chloride in peat porewater, Cussler, 1997) value of about 1·77 cm^2 day^{-1} gives a Peclet number of about 10^{-2}, indicating that molecular diffusion strongly dominates advection as the transport mechanism.

The peat–surface water interface may be poorly defined at the millimetre scale (i.e. the *z*-coordinate origin is only known to within an estimated 0·5 cm) because of the presence of a floc layer containing decomposing plant material. However, the model was developed assuming that the location is precisely known and accurately determined during porewater sampling (Duff *et al.*, 1998). Also, peat was treated as a semi-infinite media. The differential mass balance equation for one-dimensional

chemical transport in peat porewater by advection and diffusion is described by:

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \quad \text{for} \quad 0 \le z < \infty \quad (2)$$

where t is time, C is the chloride concentration in the peat porewater, u is the interstitial velocity of the peat porewater (positive downward), D_{eff} is the effective diffusion coefficient for chloride in the peat porewater (assuming that u is so small that no dispersive mixing occurs) (Krest and Harvey, 2003; Harvey *et al.*, 2004) and z is the distance into the peat from the peat–surface water interface (positive downward). The velocity u serves in this modelling application as a fitting parameter that is set to zero for the diffusion-only case. Although the actual velocity u may vary with time and depth, examining the impact of spatial and temporal variability of this parameter is beyond the scope of this work (Krest and Harvey, 2003; Harvey *et al.*, 2004). Recent results suggest that the time-averaged vertical velocities in Everglades' peat decrease with depth (Harvey *et al.*, 2005).

Observed chloride concentration within the Everglades peat at measurement times is a poorly known function of depth, $C_1(z)$. Stated mathematically as an initial condition for solving Equation (2), this condition is:

$$\text{at} \quad t = 0, \quad C = C_1(z) \quad \text{for} \quad 0 \le z < \infty \quad (3)$$

The initial concentration profile at $t = 0$ is fixed by measured porewater chloride concentrations at several depths into the peat at the starting time. For the boundary conditions used to solve Equation (2), we have specified that the surface water concentration at $z = 0$ is a known function of time $C_2(t)$, Equation (4) (determined by the transfer function derived from water level at site F4 and the chloride concentration at site U3) and that there is no chloride flux at points sufficiently deep in the peat, i.e. Equation (5)).

$$\text{at} \quad z = 0, \quad C = C_2(t) \quad \text{for} \quad t > 0 \quad (4)$$

$$\text{as} \quad z \to \infty, \quad \frac{\partial C}{\partial z} \to 0 \quad \text{for} \quad t > 0 \quad (5)$$

Chloride concentrations in the marsh surface water, which are needed for boundary condition functions, are poorly known functions of time due to the Everglades hydroperiods, the limited sample collection frequency (biweekly to monthly), and the inability to obtain samples during dry periods. A transfer function procedure was developed to estimate daily marsh surface water chloride concentrations by interpolation between observed chloride concentration measurements (see *Model parameterization*).

The analytical solution for Equations (2)–(5), developed using Laplace transform techniques and Green's functions (Churchill, 1958), is as follows:

$$C(z,t) = \frac{1}{2\sqrt{\pi D_{\text{eff}} t}} \int_0^\infty C_1(\zeta) \left[\exp\left(-\frac{(z - \zeta - ut)^2}{4 D_{\text{eff}} t} \right) \right.$$

$$\left. - \exp\left(-\frac{(z + \zeta - ut)^2 + 4\zeta ut}{4 D_{\text{eff}} t} \right) \right] d\zeta$$

$$+ \frac{1}{2\sqrt{\pi D_{\text{eff}}}} \int_0^t C_2(t - \lambda) \frac{z}{\lambda^{\frac{3}{2}}} \exp\left(-\frac{(z - u\lambda)^2}{4 D_{\text{eff}} \lambda} \right) d\lambda \quad (6)$$

where ζ and λ are the variables of integration. The first integral quantifies the contribution of the initial condition to the concentration profile. The second integral incorporates the contribution of the boundary condition. When u is set to zero, Equation (6) becomes the solution for a pure diffusion model.

For constant initial and boundary conditions, Equation (6) can be integrated analytically to yield algebraic equations relating the chemical concentration in peat porewater to depth in the peat and time. However, for a spatially variable initial condition and a temporally variable boundary condition, Equation (6) must be numerically integrated (e.g. using Simpson's rule). This integration requires functions describing the initial concentration in the peat as a function of depth, $C_1(z)$, and the concentration in the surface water as a function of time, $C_2(t)$.

The flux of chloride at the interface $J(0, t)$ due to advection and diffusion is defined as:

$$J(0, t) = -D_{\text{eff}} \left. \frac{\partial C}{\partial z} \right|_{z=0} + u\, C|_{z=0} \quad (7)$$

From Equation (6), and using Laplace transforms and Green's functions, the resulting solution for $J(0,t)$ is:

$$J(0, t) = \frac{\sqrt{D_{\text{eff}}}}{\sqrt{\pi}} \int_0^t C_2'(t - \tau) \frac{1}{\sqrt{\tau}} \exp\left(\frac{-u^2 \tau}{4 D_{\text{eff}}} \right) d\tau$$

$$- \frac{u}{2} \int_0^t C_2'(t - \tau) \text{erfc}\left(\frac{u\sqrt{\tau}}{2\sqrt{D_{\text{eff}}}} \right) d\tau + \frac{\sqrt{D_{\text{eff}}}}{\sqrt{\pi}} C_2(0) \frac{1}{\sqrt{t}}$$

$$\exp\left(\frac{-u^2 t}{4 D_{\text{eff}}} \right) - u\, C_2(0) \text{erfc}\left(\frac{u\sqrt{t}}{2\sqrt{D_{\text{eff}}}} \right)$$

$$- \frac{1}{4\sqrt{D_{\text{eff}} \pi}\, t^{\frac{3}{2}}} \int_0^\infty C_1(\zeta) \left[(\zeta + ut) \exp\left(\frac{-(\zeta + ut)^2}{4 D_{\text{eff}} t} \right) \right.$$

$$\left. + (\zeta - ut) \exp(-\frac{\zeta}{D_{\text{eff}}}) \exp\left(\frac{-(\zeta - ut)^2}{4 D_{\text{eff}} t} \right) \right] d\zeta$$

$$+ u\, C(0, t) \quad (8)$$

where τ is a variable of integration. Additional details about the numerical integration scheme used for the evaluation of Equations (6) and (8) are provided in Appendix A.

Model parameterization

Peat porewater chloride concentration profiles were calculated daily from December 1996 to January 1998 for both sites F1 and U3 for two cases: the case where only diffusion affects chloride mass transport (i.e. Equation (6) with $u = 0$), and the case where both advection and diffusion are expected to be important for mass

transport. For these calculations, values for the parameters D_{eff} and u had to be set. The value of D_{eff} was fixed at $1 \cdot 77$ cm^2 day^{-1}, the value of diffusion for chloride in water (Cussler, 1997). For the advection–diffusion model, the value of u was determined by fitting the model to data (i.e. by minimizing the porewater chloride concentration sum of the squared residuals) where the residual is the measured concentration minus the concentration calculated by the model.

Values defining the functions $C_1(z)$ and $C_2(t)$ also had to be determined for modelling the peat porewater concentration profiles. For the initial condition $C_1(z)$, peat porewater chloride concentration–depth profiles were defined based on observational data for sites F1 and U3 from 9 December 1996. The function $C_1(z)$ was determined using linear interpolation between data points to estimate the concentration in the peat porewater with depth into the peat.

Initial attempts to set the boundary condition $C_2(t)$ required a constant, average surface water chloride concentration. Model results from this approach did not compare well with the observed peat porewater concentrations. As an alternative, $C_2(t)$ was based on linear interpolation of observed chloride surface water concentration data at sites F1 and U3. Again, model results from this approach did not compare well with experimental data. However, samples for surface water chloride concentrations had only been obtained once a month at site U3 and less frequently at site F1 (Table I), and the maximum peat porewater concentration was sometimes greater than the maximum observed surface water chloride concentration. It was apparent that more temporal detail in the boundary condition was needed to reproduce the complex peat porewater chloride concentration profiles measured at sites F1 and U3. Data for surface water chloride concentrations were needed on a more frequent (daily) basis to adequately define $C_2(t)$. Consequently, a transfer function procedure was developed to estimate daily marsh surface water chloride concentrations by interpolation between observed chloride concentration measurements.

This method for defining $C_2(t)$ was based on the assumptions that: (1) the chloride concentration in marsh surface water varied as the marsh water volume increased and decreased in response to hydroperiods; (2) the marsh surface water is well mixed; and (3) the concentration in the marsh surface water was not affected by inflow of water with a different chloride concentration. We hypothesized that chloride concentrations at sites F1 and U3 were inversely proportional to surface water depth d at an alternate site F4, where daily stage data were available (Table I). Thus, at times with low water levels $C_2(t)$ was expected to be high and at times with high water levels $C_2(t)$ was expected to be low. Site F4 is about 4 miles from site U3 and is approximately midway between sites F1 and U3 (Figure 1). Changes in marsh water levels are independent of location for the sites (F1, F4 and U3) used here (McCormick *et al.*, 1996). The water levels at sites F1 and U3, which were only

measured once a month, were assumed to be similar to water levels at site F4. Water levels are equivalent at sites F4 and U3 while on three dates, water levels differed by more than $0 \cdot 5$ m between sites F1 and F4 (Figure 3a).

The direct, linear correlation between the reciprocal of marsh water depth ($1/d$) at site U3 (and F4) and the surface water chloride concentrations at site U3 was statistically significant. Surface water chloride concentration at site U3 (mg litre^{-1}) $= 12 \cdot 33$ (1/water depth at site U3 (or F4), in feet) $+ 124 \cdot 95$; $r = 0 \cdot 51497$, $n = 26$, significant at greater than the $0 \cdot 01$ level) for sampling dates from January 1996 to May 1998. However, a single regression fit of water level measurements at site F4 with the corresponding surface water chloride concentration values at site U3 exhibited poor agreement between estimated and observed surface water chloride concentrations at low water depths where the surface water chloride concentration was changing most rapidly with respect to time (Figure 3b). For this reason, a piecewise linear regression function was developed for $C_2(t)$ at site U3 (Table II). Monthly surface water chloride concentration data from site U3 which exhibited increasing concentrations with time were grouped for regression, as were data exhibiting decreasing concentrations with time. Better agreement between observed and predicted surface water chloride concentrations were obtained using these piecewise functions (Figure 3b), and thus these functions were used to define the $C_2(t)$ function in the diffusion and advection–diffusion models.

The piecewise transfer function depends on the reciprocal depth and therefore creates anomalies when depth approaches zero. Therefore, when stage value was measured at or less than zero, a value C_{max} was assigned to minimize the deviation between computed and measured porewater concentrations. Some measured water depths during dry periods reached zero at the continuously monitored site F4 (Figure 3a). Moreover, surface

Table II. Surface water chloride concentrations $C_1(t)$ at site U3 as a function of reciprocal water depth d at site F4[a]

Concentration	$C_1(t)$[b]	n[c]	R^2	Time period
Increasing	$-15 \cdot 6/d + 206$	4	$0 \cdot 1376$	04/01/96–23/04/96
Decreasing	$11 \cdot 3/d + 105$	7	$0 \cdot 1712$	24/04/96–10/10/96
Increasing	$19 \cdot 5/d + 114$	5	$0 \cdot 6408$	11/10/96–28/01/97
Decreasing	$22 \cdot 8/d + 103$	3	$0 \cdot 9673$	29/01/97–23/07/97
Increasing	$753/d - 512$	2	NA[d]	24/07/97–11/08/97
Decreasing	$316/d - 122$	3	$0 \cdot 9989$	12/08/97–07/10/97
Increasing	$60 \cdot 1/d + 65 \cdot 8$	2	NA	08/10/97–04/11/97
Decreasing	$-171/d + 351$	2	NA	05/11/97–02/12/97
Increasing	$17 \cdot 2/d + 143$	6	$0 \cdot 0970$	03/12/97–19/05/98

[a] The water depth at site F4 was used as the independent value in the correlation for estimating $C_1(t)$ for site U3 as water depth at F4 had been measured daily, but the stage at site U3 was measured once a month (Table I). This estimate for $C_1(t)$ was also used for site F1 as the surface water concentrations at site F1 were measured too infrequently to develop an expression of $C_1(t)$ specific to that site.
[b] The units of $C_1(t)$ are mg litre^{-1} and the units of d are ft.
[c] The number of data points (i.e. measurements of chloride concentration in surface water at site U3) available for each correlation.
[d] Not available.

water chloride concentrations at very low water depths have not been measured in the field, and an appropriate value of the maximum chloride concentration in surface water C_{max} is unknown. Accordingly, a limiting value of the surface water chloride concentration at very low water levels C_{max} was estimated (Table III). This was done using field data to estimate the value of C_{max} giving a minimum value for the sum of the squared residuals between calculated and field peat porewater chloride concentrations. When the stage value was reported as zero or below, the value of $C_2(t)$ was set to C_{max}.

At site F1 there were insufficient surface water chloride ion concentration measurements to correlate with stage measurements at site F4 using the linear regression method (Table I, Figure 3). Instead, we used the surface water chloride concentration boundary condition $C_2(t)$, developed for site U3 for site F1 calculations also. The value of C_{max} for site F1 was determined by optimization of the peat porewater concentration profiles for both the diffusion and the advection–diffusion models. Although less information is available for surface water chloride concentrations at site F1, and thus there is more uncertainty in the analysis, by applying this analysis to the two sites with varying amounts of information available we could examine applications for wider spatial distributions and sites with less than the optimal datasets.

Sensitivity analysis

Sensitivity analyses were completed to estimate the change in the peat porewater chloride concentration profile caused by changes in D_{eff} (fixed in the model) and by changes in u (optimized). The boundary condition function $C_2(t)$ (marsh surface water chloride concentrations over time) contributes to the model uncertainty in estimation of peat porewater chloride concentration profiles because of the lack of frequent, direct daily measurements of surface water chloride concentrations at sites F1 and U3. For the sensitivity analysis, the parameters C_{max}, D_{eff} and u were varied and the impact on the chloride concentration profile in the peat porewater was examined.

RESULTS

For initial modelling efforts, the advection velocity was set to zero to determine if a diffusion model could describe the peat porewater concentration data. Figure 5 depicts simulated chloride concentration profiles in peat porewater when only diffusion is included in the model. Although the diffusion model gave a close fit to the observed concentration profiles at site U3 for the three sampling dates, there were systematic deviations in the calculated profiles from the observed values at site F1. In a refinement of the model, the average advection velocity at each site was used as an adjustable parameter.

Porewater chloride concentration profiles were simulated using the advection–diffusion model and the calculated profiles were consistent with the values measured on three sampling dates from April 1997 through January 1998 (Figure 5). Sensitivity analysis suggests that inclusion of advective transport in the model improves the agreement between the calculated and the observed chloride concentration profiles. Agreement between calculated and observed profiles was best for site U3 (all three dates) and site F1 (July 1997 and January 1998) (Figure 5). The fit of the modelled data for site U3 (January 1998) was improved by incorporation of the advection term (Figure 5). Values of the optimized parameters ($u = -0.05$ cm day^{-1} and $C_{max} = 386$ mg litre^{-1}) for site U3 yielded profiles similar to those observed in the field (Figure 5). In particular, the advection–dispersion model describes the change in sign of the profile slope in the upper 10 cm for the April 1997 data and the levelling of the profile at 30 cm in the July 1997 data.

Regression analysis of observed and modelled peat porewater chloride concentrations was carried out to evaluate the benefit of incorporation of an advection term. The regression coefficient obtained from models either with or without an advection term for both sites F1 and U3 in July 1977 and January 1998 were highly significant ($P < 0.001$). Incorporation of an advection term changes the agreement between observed and modelled peat porewater chloride concentrations slightly.

There is deviation at the 30 and 40 cm depths of the calculated chloride concentration at site U3 in April 1997 (observed concentrations above and below the best fit estimated line) and January 1998 (observed concentrations lie above the best fit line at the 30 and 40 cm depths into the peat). In the case of site F1 there is also deviation between observed and calculated concentrations for April 1997 (observed concentrations lie below the calculated values at all depths) and January 1998 (observed concentration at 20 and 30 cm depths lie above the calculated values, as for site U3 on this date). This consistent deviation may reflect the simplifying assumption of a constant advective velocity at each site over the period of study.

Optimized values of u were -0.05 cm day^{-1} at site U3 and -0.10 cm day^{-1} at site F1. These values are similar to reported values for the sites U3 (average -0.06 cm day^{-1}, with a range of values from -0.2 to 0.3 cm day^{-1}) and F1 (average -0.17 cm day^{-1}, with a range of values from -0.6 to 0.8 cm day^{-1}) (Harvey *et al.*, 2002, Table XV and Figure 20).

The advection–diffusion model was also used to simulate peat porewater chloride concentration profiles at site F1 using the boundary condition function developed for site U3. A value of $u = -0.10$ cm day^{-1} at site F1 with $C_{max} = 400$ mg litre^{-1} gave peat porewater chloride concentration profiles similar to measured porewater values for July 1997 and January 1998. Maximum surface water chloride concentration values for site F1 were about 5% greater than the value used at site U3 (F1 $C_{max} = 405$ mg litre^{-1} for diffusion only and 400 mg litre^{-1} for the advection–diffusion case in contrast to U3 $C_{max} = 383$ mg litre^{-1} for diffusion only and 386 mg litre^{-1} for the advection–diffusion case) (Table III). The
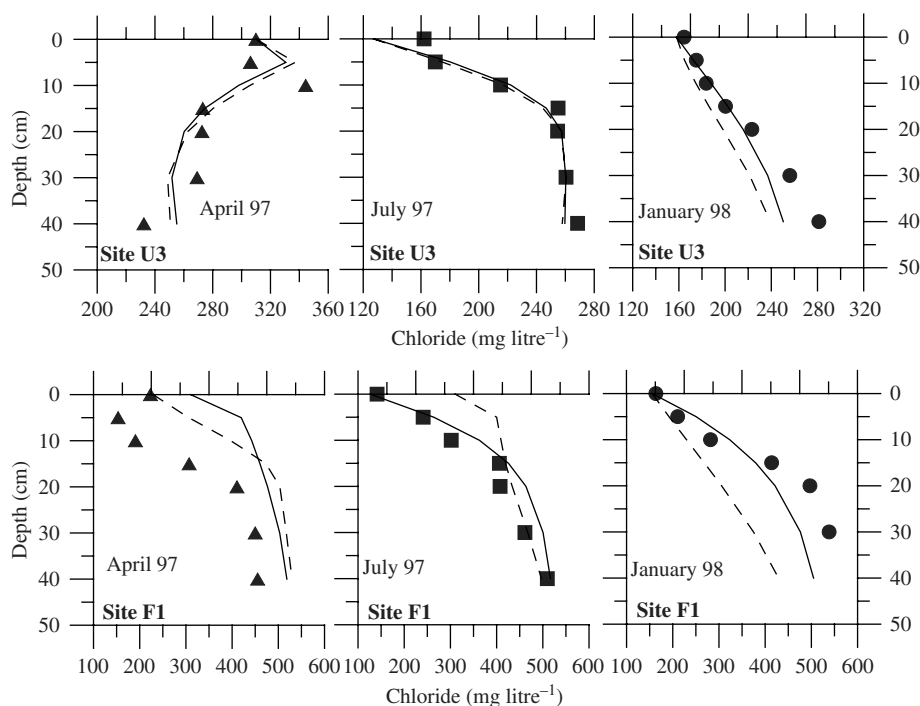
Figure 5. Measured (data points) and simulated chloride concentrations using both models for two sites and three dates. The dashed curves were calculated using the diffusion model. The solid curves were calculated using the advection–diffusion model. April 1997 is a dry period. July 1997 and January 1998 are wet periods

C_{max} values, optimized for each site with diffusion only and diffusion plus advection, vary slightly and are not significantly different at the 95% confidence level. This supports the hypothesis that addition of advective transport does not significantly influence the optimized modelling parameter C_{max}, which is to be expected in a diffusion controlled system.

Regression analysis of observed and modelled peat porewater chloride concentrations was carried out to evaluate the benefit of different modelling scenarios for each sampling site and date. Regression coefficients from this analysis yielded highly significant trends of measured versus modelled peat porewater chloride concentrations ($P < 0.001$) for samples collected at sites F1 and U3 in July 1997 and January 1998. Regression coefficients for observed and modelled peat porewater chloride concentrations at site U3 in April 1997 were slightly less significant ($P < 0.05$) and the trends were moderately significant at site F1 ($0.05 < P < 0.1$).

The predicted peat porewater chloride concentration profiles agreed less well with the measured peat porewater concentrations for site F1 than for site U3 (Figure 5). Poorer agreement between predicted and observed peat porewater concentrations at site F1 in comparison to site U3 may be due to differences in the accuracy of the chloride surface water boundary condition between the two sites. Agreement between predicted and observed peat porewater chloride concentrations was poorest for samples collected in a dry period (April 1997) and at site F1 where the boundary condition definition was the weakest.

The model represents the peat porewater chloride concentration profiles over time at site F1. However, at this site (most impacted by canal inputs), the model adjustable

parameters (Table III) ($C_{max} = 405$ mg litre^{-1}, -280 to 1080 mg litre^{-1}, diffusion; and $u = -0.10$ cm day^{-1}, -0.049 to -0.15 cm day^{-1}) have large confidence intervals indicating poorly constrained parameter values.

Sensitivity analysis

The value selected for the peat chloride D_{eff} in the model in these calculations was that of chloride ion in pure water. This is appropriate because peat porosity and tortousity will only slightly reduce D_{eff} from the pure water value. Everglades peat is about 95% water (Gilmour *et al.*, 1998). Peat solids are about 93% organic matter and, at the pH of Everglades peat porewater, peat organic matter is negatively charged as is chloride ion. Ion transport occurs in the water occupying the interstitial space between decaying organic matter fragments. Chloride exclusion from the negatively charged region near the peat surface may minimize chloride interactions with the peat matrix, possibly reducing the porosity and tortousity influences on the diffusion coefficient. Vertical transport of water and dissolved constituents out of the peat porewater due to gas ebullition may also enhance transport, increasing the apparent D_{eff} value. Sensitivity analyses varying D_{eff} suggest that the estimated peat porewater chloride concentration profiles are not strongly dependent on the value of D_{eff}. For example, doubling or halving the D_{eff} value changes only slightly the shape and magnitude of the chloride concentration profile. The difference in the measured minus estimated porewater chloride concentration using the range of diffusion coefficients ($D_{eff}/2$, D_{eff}, and $D_{eff} \times 2$) are not statistically significant. For example, using U3 data for the

21 April 1997 sampling date, the average absolute value of the difference between the measured and estimated chloride concentrations are: $D_{eff} = 1 \cdot 77$, mean absolute difference $= 17 \cdot 8$ mg Cl litre^{-1}, with 95% confidence levels of $3 \cdot 2$–$32 \cdot 3$ mg Cl litre^{-1}; $D_{eff} = 3 \cdot 4$, mean absolute difference $= 18 \cdot 2$ mg Cl litre^{-1}, with 95% confidence levels of $6 \cdot 3$–$30 \cdot 1$ mg Cl litre^{-1}; $D_{eff} = 0 \cdot 885$, mean absolute difference $= 26 \cdot 3$ mg Cl litre^{-1}, with 95% confidence levels of $2 \cdot 3$–$50 \cdot 2$. The mean absolute differences and confidence limits are similar for the other two sampling dates.

In contrast to the sensitivity analysis results for the D_{eff} parameter, sensitivity analysis results for u show that the simulated peat porewater chloride concentration profiles are sensitive to u. Both the magnitude and shape of the peat porewater concentration profiles change dramatically over the range of u from $-1 \cdot 0$ to $1 \cdot 0$ cm day^{-1}. This implies that the parameter u may be determined with reasonable accuracy from the available profile data.

The sum of squares plot versus C_{max} was similar for u values of 0, $-0 \cdot 05$ and $-0 \cdot 10$ cm day^{-1}. The C_{max} values increase about 1% with each increase of $0 \cdot 05$ in u. The C_{max} for site F1 (at $u = 0$) was about 3% greater than at site U3. Sensitivity analysis of the C_{max} term at site U3 exhibits a well-defined minimum in the sum of squares over the range of C_{max} values 300–500 mg litre^{-1}. The sum of squares fit a second order equation. The RMSE (root mean square error) was fit to a quadratic function in terms of C_{max}. The derivative of this quadratic function set to zero (that is, the minimum of the derivative RMSE function with respect to C_{max}, set equal to zero) gave the optimized C_{max} term. These results support the robustness of the C_{max} estimate.

Effects of hydroperiods on chloride flux

The relationship between hydroperiods and chloride flux at the peat–surface water porewater interface was examined by plotting the flux of the chloride concentration at the interface, $J(0, t)$ in Equation (8), as a function of time for site U3 (Figure 6).

Average daily chloride flux at site U3 over the period of study was positive (i.e. into the peat): $0 \cdot 0115$ mg cm^{-2} day^{-1}). The finding that chemical flux varies with hydroperiods is supported by the observations of others
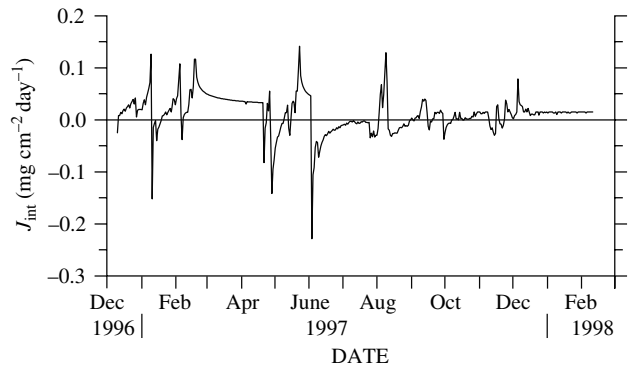

Figure 6. Plot of $J(0,t)$ as a function of time at site U3, calculated using Equation (8)

who described the influence of climate on carbon cycling (Scott *et al.*, 1998), nutrient movement (Windemuller *et al.*, 1997) in Everglades canals, and inorganic mercury concentrations (Snodgrass *et al.*, 2000).

Application of the peat porewater model to other systems

By modelling a conservative species, we have illustrated the role of the initial concentration profile, daily surface concentrations and interstitial velocity on mass transport in the Everglades. The approach to modelling chloride mass transport in peat porewater developed here can be used to study the mass transfer of other conservative chemical constituents in the Everglades. The model quantifies physical processes that describe observed peat porewater chloride concentration profiles at two sites in WCA-2A on a daily basis from April 1997 to January 1998. Peat porewater chloride concentration profiles matched observed concentration profiles during one dry period and two wet periods. Modelling of reactive constituents in this way would require modifications to this approach to include geochemical reactions. The mass balance equations for mass transfer in peat porewater, Equations (2) and (7), can be modified to include the effects of chemistry (Runkel and Bencala, 1995). Development of solute flux models for the peat–surface water interface, such as those presented here for chloride, could be useful in describing the bioavailability of contaminants and nutrients and in developing and testing hypotheses for the mechanisms involved in mass transport.

Table III. Parameters estimated using peat porewater concentration data[a]

Site	Model	Parameter	Value	95% Confidence interval
F1	Diffusion	C_{max}	405 mg litre^{-1}	-280 to 1080 mg litre^{-1}
	Advection–diffusion	C_{max}	400 mg litre^{-1}[b]	—
		u	$-0 \cdot 10$ cm day^{-1}	$-0 \cdot 049$ to $-0 \cdot 15$ cm day^{-1}
U3	Diffusion	C_{max}	383 mg litre^{-1}	300 to 466 mg litre^{-1}
	Advection–diffusion	C_{max}	386 mg litre^{-1}	376 to 396 mg litre^{-1}
		u	$-0 \cdot 05$ cm day^{-1}	$-0 \cdot 019$ to $-0 \cdot 081$ cm day^{-1}

[a] These parameters give a minimum value for the sum of the squared residuals between the model prediction of peat porewater concentrations and the observed values.
[b] The residual sum of squares did not minimize for site F1 using the advection–diffusion model with advection of $-0 \cdot 10$ cm day^{-1}. We chose 400 mg litre^{-1} as C_{max} for the calculations as a reasonable estimate.

CONCLUSIONS

It is important to incorporate as much physical and chemical data as is available at each site to best characterize the advective–diffusion process in the peat porewater system. An advection–diffusion model describes hydroperiod-related peat porewater chloride concentration fluctuations in the South Florida Water Management District's WCA-2A. In evaluating mathematical models of physical processes, it is important to recall the statistician George Box's famous quote on modelling: 'All models are wrong, but some are useful'. Models have utility and value even where they have been developed using sparse data sets. For the modelling described here, it was necessary to estimate surface water chloride concentrations in daily time steps, and it was noted that water levels and surface water chloride concentrations change with hydroperiods. Surface water chloride concentrations vary inversely with changing marsh water depth. The model developed here demonstrates that porewater chloride concentrations in the upper 60 cm of peat at two sites in WCA-2A changed in a systematic way with transition between wet and dry periods over a time interval of weeks, driven by changing surface water chloride concentrations. The model also suggests that an estimated average velocity for advective transport into or out from the peat made a small contribution to the calculated chloride concentration profiles. Chloride concentrations deeper than about 75 cm in the peat at each site were independent of hydroperiods, i.e. they were static. Chloride flux into and out from the peat is also related to marsh hydroperiods. Average daily chloride flux at site U3 over the period of study was positive, i.e. into the peat.

The major weakness in the approach outlined here is the uncertainty in the boundary condition used to specify the surface water chloride concentration. However, the approach yields some useful results. The model analysis demonstrates that the variations in chloride concentrations in surface water, due to rapidly changing water levels and concomitant changes in surface water chloride concentrations, may affect the concentrations in peat porewater and the flux of chloride between the surface water and porewater. This result may be applicable to the transport of other peat porewater dissolved constituents and highlights the importance of characterizing surface water concentrations of chemicals of interest during dry periods as well as wet periods, even if the water samples are difficult to obtain. The mathematical model developed here, describing the peat porewater chloride concentration profiles and the flux of chloride at the porewater/surface water interface, is an important tool for understanding the fluxes of conservative solutes into and out of the peat during wet and dry hydroperiods. This approach provides a physical foundation from which the benthic exchange of non-conservative (reactive) constituents can be modelled with the incorporation of independent biogeochemical processes.

APPENDIX: NUMERICAL INTEGRATION SCHEME

The integration employs an open-ended algorithm that does not require the evaluation of the integrand at the end points of the range of integration because the integrands for Equations (6) and (8) cannot be evaluated at $t = 0$.

Numerical integrations for the solution of Equations (6) and (8) were performed by splitting the interval of integration into N equally spaced subintervals and then using an open-ended Simpson's rule (Stoer and Bulirsch, 1993) expressed as the following:

$$\int_a^b f(x)\mathrm{d}x \approx \frac{h}{8}\left[3\sum_{i=0}^{3N-1} f\left(a + \frac{2i+1}{6}h\right) - \sum_{i=0}^{N-1} f\left(a + \frac{2i+1}{2}h\right)\right] \qquad (A1)$$

where $h = (b - a)/N$. Equation (A1) is evaluated for N subintervals and then again for $3N$ subintervals. Each result is an approximation for the area underneath $f(x)$. If the difference between the areas computed with $3N$ subintervals and N subintervals is less than 10^{-6} times the solution obtained for N subintervals, convergence is achieved. Otherwise, the computer evaluates the area again with three times the number of subintervals.

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