ELSEVIER

Chemical Geology 209 (2004) 271–294

CHEMICAL GEOLOGY
INCLUDING
ISOTOPE GEOSCIENCE

www.elsevier.com/locate/chemgeo

Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA

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Received 27 May 2003; accepted 10 June 2004

Abstract

Concentrations of rare earth elements (REE), major inorganic solutes, and dissolved organic carbon (DOC) were measured in waters from the Great Dismal Swamp in southeastern Virginia, including Lake Drummond (pH=4.3), and its principal surface inflows and outflow. Concentrations of REE are high in the lake (average Nd=8 nmol/kg), and the acidic DOC-rich inflow and out flow waters (i.e., Nd=12.5 nmol/kg in Jericho–Washington Ditch and ~8 nmol/kg in Feeder Ditch, respectively). The slightly acidic (pH 6–6.4) inflow waters from west of the Suffolk Scarp that comprise the chief source of surface water flow into Lake Drummond exhibit lower REE concentrations (Nd=3.4–7 nmol/kg). Great Dismal Swamp waters are all enriched in the middle REEs compared to the light and heavy REEs (LREE and HREE) when normalized to upper continental crustal (UCC) values. Rare earths are positively correlated to DOC concentrations in Great Dismal Swamp waters and inversely correlated with pH. Speciation calculations using a modified version of the well established Humic Ion-Binding Model V predict that organic matter complexes are the predominant form of dissolved REEs in Great Dismal Swamp waters despite significant competition from aqueous Fe and Al for organic matter binding sites. Adsorptive cathodic stripping voltammetry (ACSV) was employed, using a previously developed competitive ligand equilibration approach that involved adding the *o*-cresolphthalexon (OCP) ligand, to directly investigate REE complexation with natural organic ligands in Great Dismal Swamp waters. Although preliminary, the results of the ACS voltammetric titrations are consistent with dominance of organic matter complexes of REEs in Great Dismal Swamp waters. The results of the speciation modeling and the voltammetric titrations all point towards control of dissolved REEs in Great Dismal Swamp waters by complexation of these heavy metals with natural organic matter.

Keywords: Rare earth elements; Speciation; Humic substances; Geochemistry; Great Dismal Swamp; Virginia

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0009-2541/$ - see front matter
doi:10.1016/j.chemgeo.2004.06.012

1. Introduction

Understanding the chemical behavior of the rare earth elements (REEs) in natural waters is critical to their successful application as geochemical tracers in low-temperature environments, as well as for predicting their impact on, and fate and transport within, the environment. One of the most important factors affecting these and other heavy metals in natural waters is complexation with dissolved inorganic and organic ligands. It is well known, for example, that complexation reactions exert important controls on the mobility, effective solubility, reactivity, and toxicity of trace metals in the environment (e.g., Sunda and Guillard, 1976; Brand et al., 1986). Many studies have shown that the toxicity and bioavailability of transition metals are related to the concentrations of their free hydrated forms, and not their total concentrations (Sunda and Guillard, 1976; Brand et al., 1986; Coale and Bruland, 1988; Moffett et al., 1990, 1997). These investigations clearly demonstrate the biological importance of metal complexation with dissolved ligands. Other investigations have shown that solution complexation can increase the effective solubility of certain trace elements in natural waters, and consequently facilitate their transport in groundwater systems (McCarthy et al., 1998a,b). Although we are not concerned here with REE toxicity, complexation reactions involving these heavy metals are expected to strongly influence their mobility in the environment, chemical fractionation across the REE series, adsorption, and ultimately their global biogeochemical cycle. Byrne and Kim (1990) previously demonstrated, for example, that adsorption of REEs to particles coated by organic materials can lead to REE fractionation patterns similar to those reported for seawater.

Unfortunately, solution complexation involving naturally occurring organic ligands is only poorly known for most trace metals, including the REEs, in natural waters (e.g., Donat et al., 1994). Previous investigations of REE speciation in natural waters have chiefly focused on solution complexation of these trace metals with inorganic ligands (e.g., Wood, 1990; Lee and Byrne, 1992, 1993; Millero, 1992; Leybourne et al., 2000), although a number of studies have examined REE complexation with simple organic ligands (Wood, 1993; Gammons and Wood, 2000; Wood et al., 2000; Ding and Wood, 2002). Recent ultrafiltration studies strongly suggest that REEs are closely associated with natural organic matter, including colloidal organic matter, in many natural waters (e.g., Tanizaki et al., 1992; Dupré et al., 1999; Viers et al., 1997; Ingri et al., 2000). Owing to the general recognition that organic matter is likely important in the geochemistry of REEs in aquatic environments, a variety of analytical approaches have been employed to investigate complexation of REEs with purified humic materials (e.g., Maes et al., 1988; Bidoglio et al., 1991; Moulin and Tits, 1992; Dierckx et al., 1994; Franz et al., 1997). Data obtained from some of these studies have been used to calibrate computer codes that were subsequently applied to model binding of selected REEs (i.e., Eu, Tb, Dy) with humic matter (Tipping and Hurley, 1992; Tipping, 1993, 1994, 1998; Lead et al., 1998). In the current study we present REE concentration data for the organic-rich, acidic blackwaters of the Great Dismal Swamp of southeastern Virginia, USA, and argue that complexation by organic ligands dominates the biogeochemistry of REE in these waters.

2. Study site

The Great Dismal Swamp is located on the coastal plain of southeastern Virginia and northeastern North Carolina, USA, between the drainage basins for the James River to the north and Albemarle Sound to the south (Fig. 1). The Great Dismal Swamp is recognized as being the most northern “southern” type swamp on the east coast of the USA (Mitsch and Gosselink, 1993). The swamp is bounded on the west by the Suffolk Scarp, a north trending, linear structure believed to represent a paleo-marine shoreline (Fig. 1; Oaks and Whitehead, 1979). The eastern boundary is more diffuse as it merges with the many tidal creeks and waterways that define the tidewater region of Virginia and North Carolina. The swamp currently occupies an area of about 1800 km^2. Our study focuses on Lake Drummond (and its watershed), which is a shallow (~2 m deep), blackwater lake located in the northern, Virginian section of the swamp. Lake Drummond has a surface area of approximately 13 km^2, and the upland region west

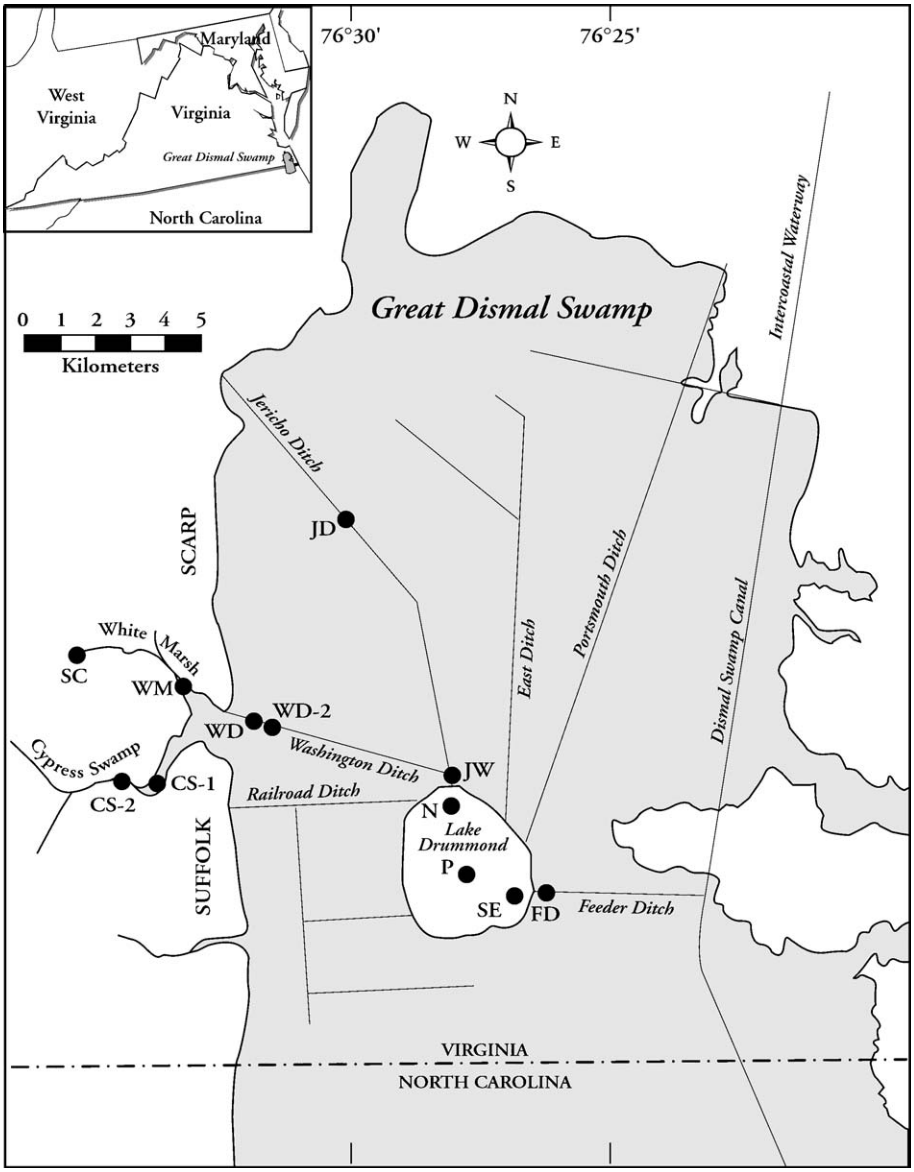

Fig. 1. Map of the study region within the Virginia portion of the Great Dismal Swamp centered on Lake Drummond. The chief source of inflow water to Lake Drummond is the Washington Ditch, which is itself fed by the Cypress Swamp and White Marsh systems west of the swamp and west of the Suffolk Scarp. Sample locations are indicated by filled circles and the following labels: SC=Skeeter Crossing; WM=White Marsh, CS-2=Cypress Swamp 2; CS-1=Cypress Swamp 1; WD=Washington Ditch; WD-2=Washington Ditch 2 (not sampled in this study); JD=Jericho Ditch; JW=Jericho–Washington Ditch; N=Lake Drummond North, P=Lake Drummond Profile (consists of three samples collected at 0.2, 1, and 2 m depths), SE=Lake Drummond Southeast; FD=Feeder Ditch.

of the lake that drains into the lake and comprises the lake's watershed, occupies roughly 98 km^2 (Lichtler and Walker, 1979; Marshall, 1979). The major surface water inflow to Lake Drummond is via the Cypress Swamp–Washington Ditch flow system, whereas the lake drains through the Feeder Ditch (Fig. 1; Lichtler and Walker, 1979). Annual precipitation at Lake Drummond is 1280 mm, and the mean annual temperature in the region varies between 15 and 15.4 °C (Lichtler and Walker, 1979).

3. Sample collection

Prior to sample collection, all sample bottles were rigorously cleaned using trace element clean procedures. Briefly, high density linear polyethylene (HDPE) and Teflon® sample bottles were first triple washed with copious amounts of distilled–deionized water (18 MΩ cm), and then placed in separate 10–20% (v/v) reagent grade nitric acid baths (Fisher Scientific) for 7 to 10 days. The sample bottles were then removed from the acid baths, rinsed three times with distilled–deionized water, and subsequently immersed in another acid bath consisting of 10–20% (v/v) trace metal grade nitric acid (Fisher Scientific) for an additional 7 to 10 days. Following this second acid bath, the sample bottles were triple rinsed with distilled–deionized water, filled with distilled–deionized water, and doubled bagged in identically cleaned polyethylene bags. During sample bottle cleaning, laboratory personnel wore clean polyethylene gloves. After sample bottles were cleaned and bagged, they were placed within a clean polyethylene box for transport to and from the field collection sites.

Surface water samples and one groundwater sample (i.e., Skeeter Crossing sample) were collected in July 2000 (July 2001 for orthophosphate samples) from Lake Drummond and its inflow and outflow streams/ditches within the Great Dismal Swamp watershed (Fig. 1). Because sampling for the bulk of the study was limited to one period in mid-summer, the resulting data cannot provide any insights into seasonal variations and biological effects on REE concentrations in these waters. The water samples were collected by pumping the water through previously cleaned Teflon® tubing using a peristaltic pump. All "surface water" samples were collected at approximately 0.2 m depth, except for two "deep" samples (1 and 2 m, respectively; Table 1) collected from roughly the middle of Lake Drummond. These two deeper samples, along with an overlying sample collected at 0.2 m, comprise a lake profile for the shallow lake (location P in Fig. 1). The Skeeter Crossing sample was collected from a partially dry stream bed after excavating a small depression in the stream bed using gloved hands. After the suspended sediments settled from the water, which immediately percolated up from below to fill the excavated depression, a water sample was collected as described above. Therefore, the Skeeter Crossing sample represents base flow (i.e., groundwater) in this small stream.

Each water sample was immediately filtered (at the time of collection) through in-line filter capsules (Gelman Sciences, 0.45 μm, polyether sulfone membrane), and into pre-cleaned HDPE sample bottles. Each sample bottle was triple rinsed with the filtered water sample before the bottle was filled with the actual sample. The samples for total quantification of the REEs were subsequently immediately acidified to pH<2 with ultrapure nitric acid (Seastar Chemicals), doubled bagged in pre-cleaned polyethylene bags, and returned to the laboratory for analysis. Major cation and anion samples were collected identically, except the anion samples were not acidified, and only a drop of ultrapure nitric acid was used to preserve the cation samples (e.g., Welch et al., 1996). Temperature and pH for each sample were measured on site, and alkalinity was determined in the field (i.e., Skeeter Crossing, Cypress Swamp 1 and 2, White Marsh, Washington Ditch) or in the laboratory (Lake Drummond, Jericho–Washington Ditch, Feeder Ditch) using standard alkalinity titration method. For the Jericho Ditch sample, we only measured field parameters (temperature, pH) and collected a sample for DOC determination. Water samples for dissolved organic carbon (DOC) determination were filtered as above, collected in pre-cleaned glass vials, and immediately returned to the laboratory for analysis.

Water samples for adsorptive cathodic stripping voltammetric (ACSV) determination of La concentrations, and for evaluating La speciation with naturally occurring organic ligands, were collected from the Washington Ditch sampling location (Fig. 1) during April and May of 2001. The ACSV samples were collected identically to those obtained the previous summer except that pre-cleaned Teflon® sample bottles were used instead of HDPE, and the sample aliquots for the speciation titrations were not acidified. Following their collection, the samples were immediately returned to the laboratory for analysis, which was always conducted within 2 days of collection. Aliquots of the samples to be used for quantification of total dissolved La concentrations were UV-oxidized to destroy all organic complexes, which would otherwise interfere with the measurement. These aliquots were UV-oxidized (1.2 kW Hg-

Table 1
Major solute composition (in mmol/kg) for surface waters from the Great Dismal Swamp, southeastern Virginia, USA

	Washington Ditch	Cypress Swamp 1	Cypress Swamp 2	White Marsh	Skeeter Crossing	Jericho Ditch	Jericho–Washington	Feeder Ditch	Lake Drummond Southeast	Lake Drummond 0.2 m	Lake Drummond 1 m	Lake Drummond 2 m	Lake Drummond North
Ca	0.144	0.227	0.220	0.136	0.464	NM	0.141	0.108	0.110	0.116	0.115	0.115	0.111
Mg	0.063	0.081	0.077	0.060	0.196	NM	0.043	0.038	0.039	0.041	0.040	0.040	0.040
Na	0.224	0.190	0.188	0.225	0.204	NM	0.193	0.177	0.183	0.183	0.213	0.186	0.181
K	0.065	0.075	0.073	0.064	0.138	NM	0.043	0.041	0.042	0.042	0.043	0.045	0.041
Li[a]	6.85	48.3	47.1	6.63	27.5	NM	0.359	27.0	0.411	0.447	0.533	0.390	ND
Cl	0.283	0.267	0.257	0.284	0.799	NM	0.247	0.249	0.250	0.253	0.255	0.251	0.249
Alk[b]	0.172	0.360	0.136	0.168	0.176	NM	0.104	0.064	0.08	0.088	0.072	0.064	0.064
SO_4	0.135	0.178	0.184	0.110	0.270	NM	0.039	0.044	0.045	0.045	0.045	0.045	0.043
NO_3	0.011	0.029	0.032	0.017	0.287	NM	0.008	0.016	0.012	0.015	0.017	0.019	0.015
F	0.003	0.005	0.007	0.003	0.011	NM	0.001	0.001	0.002	0.001	0.001	0.002	0.001
PO_4[a]	NM	1.06	1.21	0.52	0.18	NM	1.41	0.92	0.42	0.42	NM	NM	1.41
DOC[a]	1030	1031	952	1040	445	9600	6304	5109	4463	4442	5116	4966	4500
pH	6.18	6.42	6.28	6.32	6.4	3.61	4.22	4.31	4.3	4.31	4.33	4.33	4.33
Temp (°C)	22.37	24.2	24.4	24.9	19.5	19.7	21.5	28.5	28.5	27.6	28	27.9	28.6

NM=not measured; ND=not detected.

Dissolved organic carbon (DOC), PO_4, and Li concentrations are in μmol/kg.

[a] In μmol/kg.

[b] As HCO_3.

arc lamp) for at least 12 h, after which they were ready for total La quantification. Aliquots for the La speciation titrations were not UV-oxidized.

4. Sample and data analysis methods

4.1. Major solutes and DOC

Major cations and anions were determined in each water sample using ion chromatography (Dionex DX-500) following standard methods (e.g., Welch et al., 1996). Anions (Cl^-, SO_4^{2-}, NO_3^-, F^-) were determined using Ion Pac AS11 and AG11 columns, ASRS-ULTRA (4 mm) self-regenerating anion suppressor, an EG-40 eluent generator, and MilliQ water (18 MΩ cm) as the reagent. Cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Li^+) were measured with Ion Pac CS12A and CG12A columns, a CSRS-ULTRA (4 mm) self-regenerating cation suppressor, and 20 mM methane sulfonic acid (MSA) as the reagent. Soluble reactive phosphate (i.e., orthophosphate) was measured by visible light spectrometry (Spectronics® Genesys™ 5 UV spectrophotometer) using the molybdenum blue method (Murphy and Riley, 1962). Dissolved organic carbon (DOC) concentrations were measured by high temperature catalytic oxidation (HTCO) using a Shimazdu TOC-5000 total carbon analyzer (Burdige and Gardner, 1998).

4.2. Total dissolved (<0.45 μm) REE concentrations

Rare earth element concentrations were determined by inductively coupled plasma mass spectrometry (Perkin Elmer Elan 6000) at the University of Alabama following methods discussed previously (Stetzenbach et al., 1994; Graham et al., 1996; Hodge et al., 1998). In brief, each water sample was introduced to the ICP-MS using a cross-flow nebulizer without preconcentration (Graham et al., 1996). The REE isotopes ^{139}La, ^{140}Ce, ^{142}Ce, ^{141}Pr, ^{143}Nd, ^{146}Nd, ^{148}Sm, ^{149}Sm, ^{152}Sm, ^{151}Eu, ^{153}Eu, ^{157}Gd, ^{158}Gd, ^{159}Tb, ^{161}Dy, ^{163}Dy, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{167}Er, ^{169}Tm, ^{172}Yb, ^{173}Yb, ^{174}Yb, and ^{175}Lu were used to quantify the REEs in the water samples. Although, many of these REE isotopes are free of isobaric interferences, it is advantageous, when possible, to monitor multiple isotopes of a particular element as an additional check of isobaric interferences (e.g., Hodge et al., 1998). Measured $REEO^+/REE^+$ ratios were ordinarily <1%, and for those that were >1%, appropriate corrections were made (Stetzenbach et al., 1994; Graham et al., 1996).

The ICP-MS was calibrated and the sample concentrations verified using a series of REE calibration standards of known concentrations (0.1, 2, 10, 100, 250, 500, and 1000 ng/kg). The calibration standards were prepared from NIST traceable High Purity Standards (Charleston, SC). Check standards prepared from Perkin Elmer multi-element solutions were analyzed regularly during the analyses to certify accuracy (e.g., Graham et al., 1996; Hodge et al., 1998). In addition, ^{115}In was added to each sample as an internal standard (Graham et al., 1996). Detection limits were in the low pmol/kg level for all REEs (Table 2). Analytical precision, except for Eu, was typically better than 5% RSD (relative standard deviation), and better than 1% RSD for La, Ce, Nd, and Yb. Nevertheless, for Eu the precision was always better than 10% RSD.

4.3. Adsorptive cathodic stripping voltammetry (ACSV)

Wang et al. (1985) developed an extremely sensitive ACSV technique for measuring total dissolved REE (i.e., La, Ce, and Pr) concentrations in water samples using adsorptive accumulation of the REE *o*-cresolphthalexon (OCP) complex on a hanging mercury drop electrode (HMDE). The added ligand in this case, OCP, is an organic dye, and is a derivative of phenolphthalein (Gao and Zhang, 1984). Wang et al.'s method was used as a starting point for developing a competitive ligand equilibration adsorptive cathodic stripping voltammetric (CLE/ASCV) technique to investigate REE speciation with naturally occurring organic ligands. Similar methods have proven effective in quantifying organic speciation of transition metals in natural waters (e.g., van den Berg, 1984; Donat and van den Berg, 1992; Mota and Correia dos Santos, 1995; and references therein).

The method as presented by Wang et al. (1985) was only communicated as a technique for measuring La, Ce, and Pr concentrations in laboratory prepared aqueous solutions, and had not been tested on natural

Table 2
Rare earth element concentrations (in pmol/kg) for surface waters from the Great Dismal Swamp, southeastern Virginia, USA

	Washington Ditch	Cypress Swamp 1	Cypress Swamp 2	White Marsh	Skeeter Crossing	Jericho–Washington	Feeder Ditch	Lake Drummond Southeast	Lake Drummond 0.2m	Lake Drummond 1m	Lake Drummond 2m	Lake Drummond North	Blank
La	7456	4336	2981	4986	12,521	9302	5676	4765	4862	6680	6347	5329	<1.14
Ce	17,211	11,588	7900	11,835	27,347	24,024	13,826	12,728	13,033	16,939	15,971	13,821	<0.48
Pr	1707	1167	852	1361	3040	2919	1837	1699	1734	2234	2097	1903	<1.89
Nd	7135	4762	3447	4938	11,734	12,505	7809	6991	7245	9084	8898	7253	<2.88
Sm	1297	914	676	1049	2252	2446	1584	1457	1523	1872	1807	1484	3.65
Eu	ND	ND	ND	ND	ND	193	49.3	27.2	47.3	101	89.9	29.1	<0.79
Gd	1325	949	708	1081	2351	2453	1560	1464	1506	1869	1819	1525	2.09
Tb	172	123	91.4	139	295	320	202	185	191	242	230	188	<0.42
Dy	889	654	494	731	1526	1647	1028	969	1023	1256	1220	993	<1.59
Ho	158	114	93.0	133	283	306	195	183	197	237	229	190	<0.65
Er	450	327	270	378	785	889	573	539	577	696	682	572	<1.17
Tm	60.1	42.9	36.7	50.7	99.5	118	78.4	75.5	80.9	96.6	91.4	78.6	0.5
Yb	353	270	221	293	601	729	483	474	516	602	581	498	<1.65
Lu	52.1	39.6	33.5	44.2	91.1	110	74.0	72.9	77.6	91.1	86.9	76.6	<0.6
Gd/La[a]	1.59	1.96	2.12	1.94	1.68	2.36	2.46	2.75	2.75	2.50	2.56	2.56	
Gd/Lu[a]	1.92	1.81	1.60	1.85	1.95	1.60	1.59	1.52	1.55	1.55	1.58	1.51	
La/Lu[a]	1.21	0.926	0.752	0.954	1.16	0.719	0.649	0.553	0.621	0.621	0.619	0.589	
Yb/Nd[a]	0.701	0.804	0.911	0.842	0.726	0.826	0.877	0.960	0.940	0.940	0.925	0.974	
Eu/Eu[a]						−0.44	−0.84	−1.07	−0.84	−0.60	−0.64	−1.05	

Eu/Eu*=log{$2Eu_{UCC}/[Sm_{UCC}+Gd_{UCC}]$}.
ND=Not detected.
For Blank, < indicates that value was less than the limit of detection that is shown.
[a] UCC-Normalized Ratios, where UCC is upper continental crust (Taylor and McLennan, 1985).

water samples. We chose La for our experiments because after Ce, it is the most abundant REE, but unlike Ce, it does not have its own redox chemistry. Our approach was essentially identical to that described by Wang et al. (1985), except that we employed a different buffer for the low pH Great Dismal Swamp waters. The buffer used by Wang et al. (1985), NH_3/NH_4Cl, has a pK_a of 9.3, and thus has an effective working pH range of roughly 8.3 to 10.3, which is too high for Great Dismal Swamp waters (Table 1). However, the MES buffer (i.e., 2-[*N*-morpholino]ethanesulfonic acid; pK_a 6.1) was found to give sufficient sensitivity for detection of La at the low nanomolar levels in these mildly acidic swamp waters (i.e., Washington Ditch, pH 6.2; Table 2). Furthermore, by lengthening the adsorptive accumulation (i.e., "preconcentration") time allowed for the La–OCP complex to adsorb to the HMDE, Wang et al. (1985) demonstrated that the method detection limit could be significantly improved. For preconcentration times of 0.5 and 4 min, for example, the detection limits for the REEs were 25 and 2.5 nM, respectively, whereas for a preconcentration time of 20 min detection limits for La, Ce, and Pr were on the order of 0.1 to 0.2 nM (Wang et al., 1985). Consequently, preconcentration times of between 15 and 20 min were used for our La measurements.

The ACSV analysis was performed by standard additions, whereby aliquots of the UV-oxidized Washington Ditch samples were placed into a series of Teflon® cups of increasing La concentrations along with the MES buffer and the OCP ligand. The added OCP forms a dissolved complex with La, and the La–OCP complex is subsequently adsorbed (under the influence of an applied potential) onto the surface of a hanging mercury drop electrode (HMDE) for detection. After an appropriate adsorption time (depending upon the La concentration in the sample), the adsorbed La–OCP complex is then stripped off the HMDE by increasing the applied potential in the negative direction. The current generated during this stripping step is proportional to the concentration of La in the sample (J.R. Donat, 2000, pers. comm.). After determining the total dissolved La concentration in the sample, a second titration was performed on an identical set of Teflon® cups as above, except the non-UV-oxidized Washington Ditch samples were used in place of the UV-oxidized aliquots. This second titration was undertaken to evaluate the possibility that La was organically complexed in Great Dismal Swamp waters.

4.4. Speciation modeling

Because the waters of the Great Dismal Swamp are characterized as organic-rich, acidic blackwaters, it is highly likely that REEs are complexed by naturally occurring organic ligands in these waters. Indeed, a previous study of REEs in broadly similar waters strongly suggests that REE geochemistry is controlled by the association of these trace metals with organic matter (i.e., Viers et al., 1997). Consequently, to appropriately model REE speciation in Great Dismal Swamp waters, it is necessary to consider REE complexation with both inorganic and organic ligands. Although calculating REE speciation with inorganic ligands is a relatively simple task, modeling REE complexation with natural organic ligands is complicated by many factors, including the typical poor characterization of highly variable, natural organic matter (e.g., Thurman, 1985; Tipping, 2002). It is especially difficult, for example, to assign discrete equilibrium constants for each possible complexation reaction that can occur for large, natural organic molecules like humic and fulvic acids because of the many chemically different metal binding sites (Crawford, 1996). Furthermore, establishing activity coefficients for these ligand sites, as well as metals complexed to these sites, as a function of ionic strength is a perplexing issue that remains to be satisfactorily resolved. Nonetheless, sophisticated, discrete-site electrostatic organic complexation models have successfully been employed to model metal–organic matter complexation in natural waters (Lead et al., 1998; Glaus et al., 2000; Hummel et al., 2000; Tipping et al., 2002). Here, we employ a version of Humic Ion-Binding Model V, originally developed by Tipping and co-workers (Tipping and Hurley, 1992; Tipping, 1993, 1994). We modified the model to allow for predictions of organic and inorganic ligand complexation of all 14 naturally occurring REEs in natural waters (Tang and Johannesson, 2003). Model V was chosen because most of the important model parameters (i.e., n_A, pK_A, pK_B, ΔpK_A, ΔpK_B, P, f_{pr}, pK_{MHB}) have been determined and fixed separately for humic and fulvic acids, and because the model has been widely validated for many trace elements including some of the REEs (see Tipping, 1993; Lead et al., 1998). As a result, only a single parameter, pK_{MHA}, is required to fit model predictions to metal binding data (Tipping, 1993). The pK_{MHA} parameter represents intrinsic equilibrium constants for metal–proton exchange reactions for type A sites (see Tipping, 2002; Tang and Johannesson, 2003 for details).

The pK_{MHA} values for each of the 14 naturally occurring REEs were estimated using linear free-energy expressions developed from the pK_{MHA} values for other trace elements in the Model V database, and first hydrolysis constants and complexation constants for these metals with lactic and acetic acid (Martell and Smith, 1977; Tang and Johannesson, 2003). In addition, we further modified the Model V database by including recently determined stability constants for REE complexation with inorganic ligands (Lee and Byrne, 1992, 1993; Millero, 1992; Klungness and Byrne, 2000; Luo and Byrne, 2000). Although Model V was recently updated (i.e., Model VI; Tipping, 1998), the new code does not produce significantly different REE speciation results compared to Model V (Lead et al., 1998).

5. Results

5.1. Major ion composition

Major ion chemistry of the Great Dismal Swamp water samples are presented in Table 1 along with the corresponding pH, temperature, and DOC concentrations. All waters from the Great Dismal Swamp watershed are acidic; pH values range from a low of 3.6 for the Jericho Ditch sample to 6.4 for the Skeeter Crossing groundwater sample (Table 1). In general, waters draining the region to the west of the Suffolk Scarp (i.e., Skeeter Crossing, White Marsh, Cypress Swamp 1 and 2, Washington Ditch), and consisting of the chief inflow waters to Lake Drummond, have higher pH values (by ~2 pH units) than waters east of the Suffolk Scarp that are within the swamp proper (i.e., Jericho Ditch, Jericho–Washington Ditch, Lake Drummond, Feeder Ditch; Table 1, Figs. 1 and 2). The principal exception is the Washington Ditch sample, which was collected just east of the scarp but may be considered along with the other inflow samples based on its chemical composition.

Dissolved organic carbon concentrations are high in Great Dismal Swamp waters, and vary from a low of 445 μmol/kg for the Skeeter Crossing groundwater sample up to 9600 μmol/kg in Jericho Ditch (Table 1). Similar to pH, waters from the study area exhibit two populations in terms of their DOC concentrations. Waters from west of the Suffolk Scarp have substantially lower DOC concentrations than waters from east of the scarp, and within the swamp proper (Table 1, Fig. 2). For example, the mean (±standard deviation) DOC concentration of the inflow waters (Skeeter Crossing, White Marsh, Cypress Swamp 1 and 2, Washington Ditch) is 900±257 μmol/kg, whereas the mean DOC (±standard deviation) for the waters east of the Suffolk Scarp is 5563±1741 μmol/kg, or more than a factor of 6 greater than in the inflow waters.

In terms of major dissolved inorganic solutes, Great Dismal Swamp waters are dilute Ca–Cl–SO_4–HCO_3 waters west of the Suffolk Scarp, and typically dilute Na–Ca–Cl waters within the Lake Drummond portion of the swamp (Table 1). Although the dissolved concentrations of inorganic solutes are low in Great Dismal Swamp waters, the outstanding characteristics of these waters are their high DOC concentrations, yellow-brown color, and low pH.

5.2. REE concentrations and UCC-normalized fractionation patterns

Fig. 3 shows Nd and Yb concentrations for waters of the Great Dismal Swamp plotted as a function of pH, along with Nd and Yb values extracted from the literature for numerous other terrestrial waters (see Johannesson and Hendry, 2000 for sources of these data). For Great Dismal Swamp waters, Nd concentrations range from 3447 to 12,505 pmol/kg, and exhibit a mean (±standard deviation) of 7650±2667 pmol/kg (Table 2). Ytterbium concentrations range from 221 to 729 pmol/kg, with a mean (±standard deviation) of 468±155 pmol/kg (Table 2). Great Dismal Swamp waters have REE concentrations within the range reported, and/or orders of magnitude lower than, most acidic waters plotted in Fig. 3.

Fig. 4 is a standard plot of REE concentrations for Great Dismal Swamp waters normalized to upper

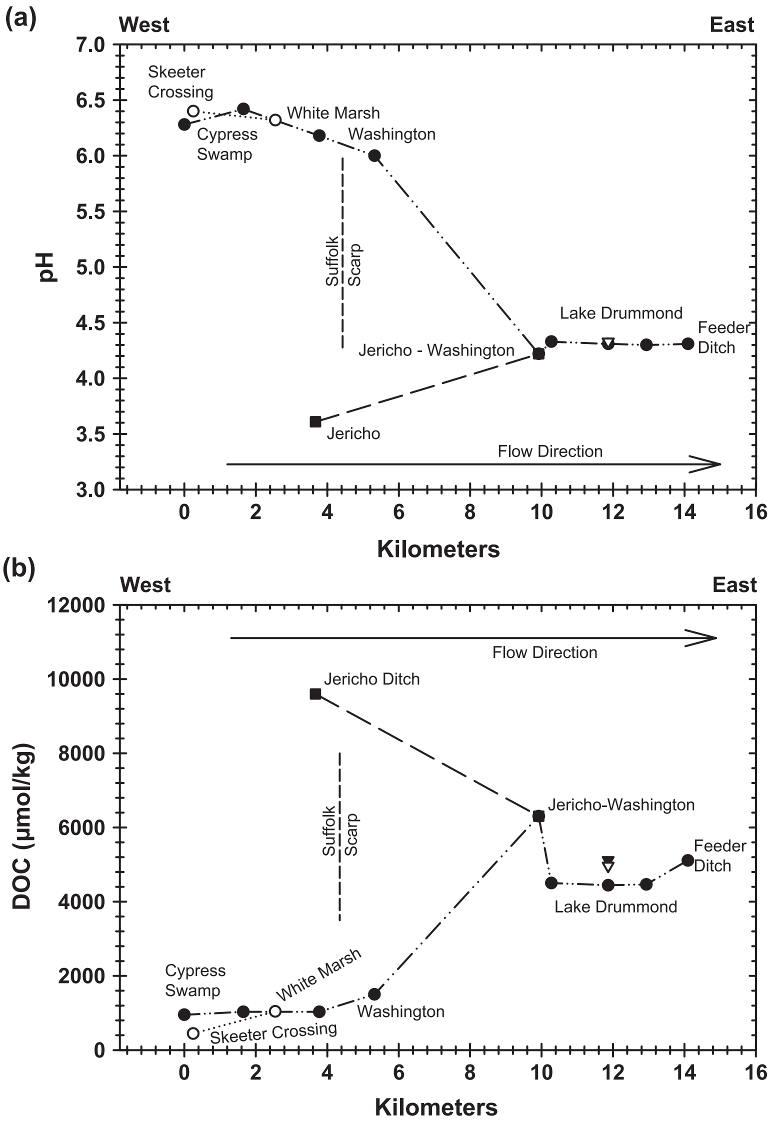

Fig. 2. Variation of (a) pH and (b) dissolved organic carbon (DOC in µmol/kg) versus distance (in kilometers) along the general flow path of surface waters. Approximate location of the Suffolk Scarp is indicated. The Jericho Ditch sample represents waters that are not directly part of the White Marsh–Cypress Swamp inflow system. The Lake Drummond profile samples are shown as inverted triangles (open symbol=1 m, and filled symbol=2 m depth).

continental crustal (UCC) values (Taylor and McLennan, 1985). It is necessary to mention that UCC and shale composites (e.g., North American Shale Composite; NASC) have similar relative REE distributions, with UCC values being on average a factor of ~20% lower than NASC values (Taylor and McLennan, 1985). Hence, normalization of REE data to either will produce relatively similar REE fractionation patterns, albeit, shifted to higher values when normalized to UCC compared to normalization to NASC. Great Dismal Swamp waters exhibit enrichments in the middle REEs (MREE; Sm, Gd, Tb, Dy) compared to the LREEs (La, Ce, Pr, Nd) and HREEs (Ho, Er, Tm, Yb, Lu) when normalized to UCC (Fig. 4). The degree of MREE enrichment is demonstrated by the UCC-normalized Gd/La and Gd/Lu ratios,

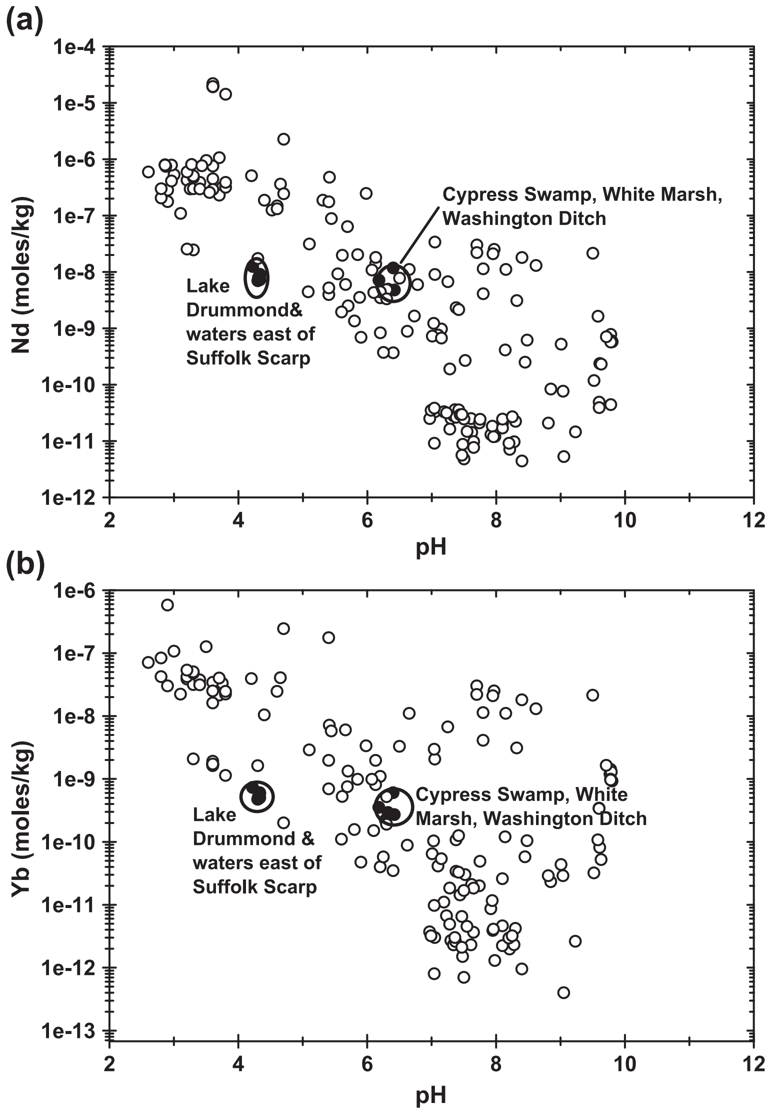

Fig. 3. Neodymium (a) and ytterbium (b) concentrations (in moles/kg) for natural waters versus pH. Lake Drummond and swamp waters from east of the Suffolk Scarp, as well as the inflow waters of the White Marsh–Cypress Swamp inflow system are shown. Sources of the data for other natural waters shown are summarized by Johannesson and Hendry (2000).

which are all greater than unity (Table 2). Except for the Skeeter Crossing groundwater sample, the UCC-normalized enrichment in the MREE over the LREE is consistently greater than the UCC-normalized enrichment of MREE over the HREEs (Table 2, Fig. 4). The mean (±standard deviation) of the UCC-normalized Gd/La ratios for all samples is 2.27±0.4, whereas for the UCC-normalized Gd/Lu ratios the mean (±standard deviation) is 1.67±0.16. It is important to note that enrichments in the MREEs have also been reported for other acidic natural waters (e.g., Elderfield et al., 1990; Sholkovitz, 1995; Sholkovitz et al., 1999; Gimeno et al., 2000). The water samples for which Eu was determined (i.e., waters from east of the Suffolk Scarp) all exhibit substantial negative UCC-normalized Eu anomalies that range from −1.07 to −0.44 (Fig. 4, Table 2).

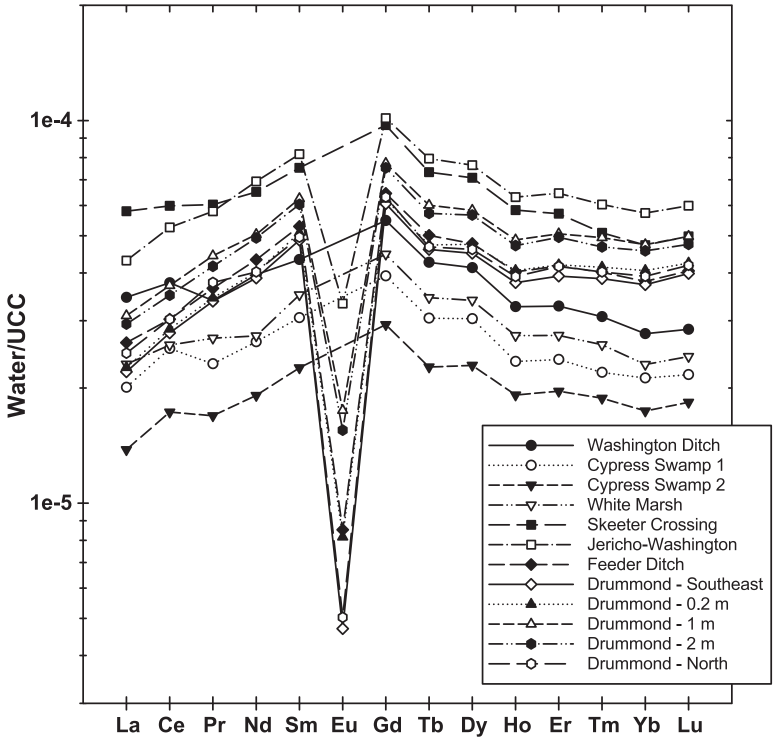

Fig. 4. Upper continental crust (UCC) normalized REE patterns for waters (i.e., Waters/UCC) from the Great Dismal Swamp. Here, the dissolved REE concentrations measured in Great Dismal Swamp waters are normalized to the corresponding UCC values, which are from Taylor and McLennan (1985).

5.3. Adsorptive cathodic stripping voltammetry

The results of the ACSV titration of UV-oxidized Washington Ditch water (collected in spring 2001) yielded a total dissolved La concentration of 5.5 nmol/kg for the Washington Ditch water. This value is similar to, albeit, 30% lower than the La concentration measured by ICP-MS for the July 2000 Washington Ditch sample (i.e., ~7.5 nmol/kg; Table 2). The difference noted could reflect differences in the analytical methods or dilution of Washington Ditch water from abundant spring rains. It is important to point out that to the best of our knowledge this ACSV-measured La concentration is the first such measurement for natural water, and demonstrates the utility of the ACSV technique for quantifying REEs in natural waters at ultra low concentrations.

Results of a CLE/ACSV titration performed on the non-UV-oxidized Washington Ditch aliquots are shown in Fig. 5. Fig. 5 demonstrates that the La

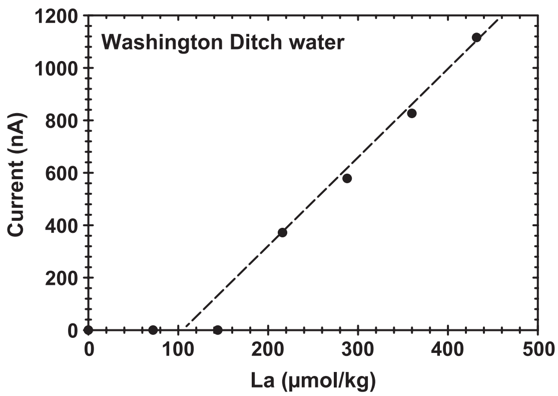

Fig. 5. An example of preliminary results for competitive ligand equilibration adsorptive cathodic stripping voltammetric (CLE/ASCV) titration for non-UV oxidized Washington Ditch waters using our modifications of the method developed by Wang et al. (1985). Note the initial suppression of the analytical response for the first three samples. We interpret this as evidence that La is entirely complexed with natural organic ligands in Washington Ditch waters. Extrapolation of the linear portion of the data back to the abscissa suggests that the La binding capacity of the natural organic matter is on the order of ~100 to ~140 μmol/kg. See text for discussion.

signal is initially suppressed, and further, an analytical response was not observed in the non-UV-oxidized Washington Ditch water samples until more than 140 μM of La had been added to the sample. The results of the titration indicate that La is organically complexed in Washington Ditch water. Furthermore, the titration data suggest that the natural organic ligands in this water sample can complex between ~100 and ~140

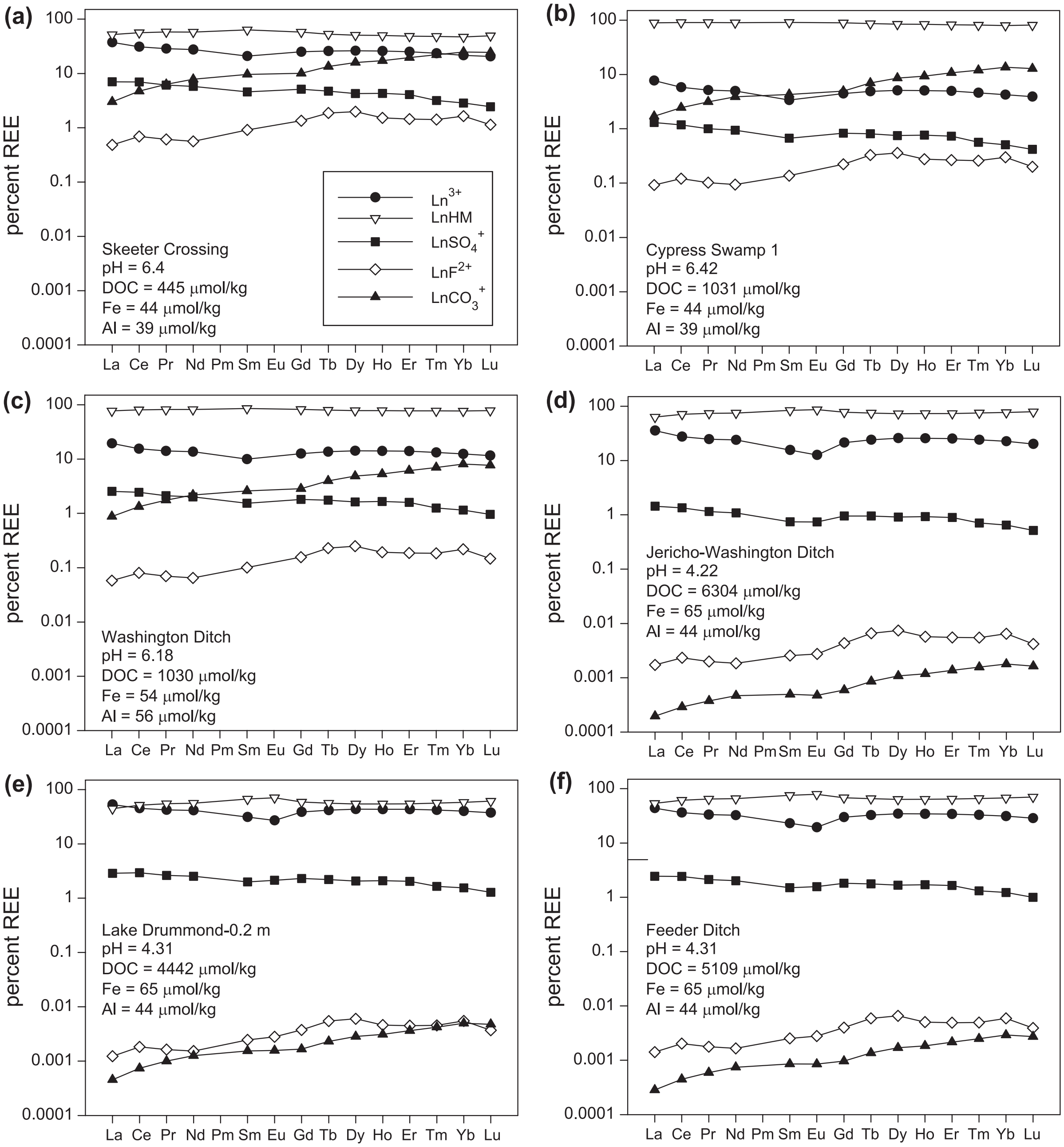

Fig. 6. Results of Humic Ion-Binding Model V (i.e., Tipping, 1994) speciation calculations for selected waters from the Great Dismal Swamp, Virginia. Dissolved Fe and Al data are from Kane (2000). See text for discussion.

μM of La before all the complexing sites are saturated with La. Although more study is required to better constrain these measurements, the outstanding feature of these data is that they represent the first direct, analytical measurements indicating REEs are complexed by naturally occurring organic ligands in a natural water sample.

5.4. Speciation model results

The results of the speciation modeling for REEs in Great Dismal Swamp waters are shown in Fig. 6. Owing to the similarity of the predicted speciation results for the waters of the Great Dismal Swamp watershed, only the results for 6 of the 12 samples collected are shown in Fig. 6. Furthermore, although we have not measured dissolved Fe or Al in Great Dismal Swamp waters, other investigators have clearly demonstrated that both compete effectively with REEs for organic matter complexation sites, as well as for inorganic ligands (e.g., Tanizaki et al., 1992; Dupré et al., 1999; Tipping et al., 2002; Tang and Johannesson, 2003). Consequently, in order to account for the effect of dissolved Fe and Al on REE speciation we used recently reported values for these metals in Great Dismal Swamp waters (i.e., Kane, 2000) in our model calculations. Specifically, the mean Fe and Al concentrations (44 and 39 μmol/kg, respectively) for seven samples from the Pocosin Swamp of Kane (2000), which corresponds to the White Marsh and Cypress Swamp regions in Fig. 1, were used for our Model V calculations for the Skeeter Crossing, both Cypress Swamp, and the White Marsh samples. Kane (2000) reports Fe and Al concentrations of 54 and 56 μmol/kg, respectively, for Washington Ditch water. Finally, the mean Fe and Al concentrations (65 and 44 μmol/kg, respectively) for Lake Drummond waters (Kane, 2000) were employed to evaluate the impact of these metals on REE speciation in our Lake Drummond samples, as well as the Jericho–Washington and Feeder Ditch samples (Fig. 6).

Model V predicts that essentially all dissolved REEs in waters of the Great Dismal Swamp are complexed with natural organic matter (Fig. 6). Specifically, Model V predicts that the percentage range of REEs bound to natural organic matter is 47–58%, 80–91%, 77–85%, 63–87%, 44–71%, and 54–79% for the Skeeter Crossing, Cypress Swamp 1, Washington Ditch, Jericho–Washington Ditch, Lake Drummond, and Feeder Ditch waters, respectively (Fig. 6). In addition, the model predicts that any REE not bound to organic ligands would likely occur in solution as free metal ions, and to a lessor extent sulfate complexes. Furthermore, the model predicts that the percentage of the free metal species occurring is substantially greater in the low pH waters (pH 4.3) east of the Suffolk Scarp compared to the more neutral pH waters to the west of the scarp (Fig. 6). The fact that free metal ions are predicted to be substantially more important in the more acidic swamp waters reflects competition of REEs with protons, as well as Fe and Al, for ligand binding sites. For example, in the case of the lower pH (4.2–4.3) waters east of the Suffolk Scarp, hydrogen ion activities are roughly 100 times greater, on average, than for the higher pH inflow waters (Table 1). Consequently, the concentration of deprotonated ligand sites that can bind REEs, Fe, and Al to the natural organic matter present will be significantly lower in the more acidic swamp waters east of the Suffolk Scarp compared to the inflow waters. It is important to note that Model V also predicts that carbonato complexes ($LnCO_3^+$) account for significant percentages of the REEs, especially the HREEs, in the more neutral pH inflow waters (i.e., Skeeter Crossing, Cypress Swamp 1 and 2, White Marsh, Washington Ditch; Fig. 6). Finally, to a first approximation, the speciation model predictions are consistent with the CLE/ACSV measurements for La in Washington Ditch waters (Fig. 5). That is, both techniques suggest that La and the REEs in general, occur predominantly as organic complexes in these waters.

6. Discussion

6.1. pH and organic matter controls on dissolved REEs

As mentioned above, Great Dismal Swamp waters are acidic and pH decreases along the flow direction from west of the Suffolk Scarp towards the east and into the swamp (Figs. 1 and 2; Table 1). Dissolved organic carbon concentrations also generally increase along the flow direction, the chief exception being at the confluence of the Jericho and Washington Ditches where the lower DOC values of Washington Ditch waters act to dilute those from the Jericho Ditch. From Figs. 1 and 2 it is clear that Jericho Ditch water contributes significantly to the high DOC concentrations of Lake Drummond and waters down stream (i.e., the Feeder Ditch). The high DOC of Jericho Ditch water has been attributed to the thicker peat deposits underlying the swamp in this region (Lichtler and Walker, 1979). Waters collected down stream of the confluence of the Jericho and Washington Ditches (i.e., Jericho–Washington Ditch, Lake Drummond, Feeder Ditch samples) not only have higher DOC values, but also exhibit substantially lower pH values than those up gradient along the Cypress Swamp–Washington Ditch part of the drainage (Fig. 2). Hence, mixing of organic acid-rich waters from the Jericho Ditch with those of the Washington Ditch likely contributes to producing the low pH waters of the Jericho–Washington Ditch, Lake Drummond, and the Feeder Ditch samples (e.g., Lichtler and Walker, 1979).

Previous investigators have demonstrated that the concentrations of dissolved REEs are strongly influenced by pH (e.g., Goldstein and Jacobsen, 1987; Elderfield et al., 1990). In general, an inverse relationship has been reported between pH and dissolved REE concentrations in natural waters, and this relationship is also exhibited by waters of the Great Dismal Swamp watershed (Fig. 3). If the Skeeter Crossing groundwater sample is neglected (see below), moderate to strong correlation coefficients (i.e., r) are calculated between pH, DOC, and individual REEs in Great Dismal Swamp waters. For example, correlation coefficients for Nd, Gd, and Yb versus pH are −0.74, −0.79, and −0.89, respectively, whereas those for Nd, Gd, and Yb versus DOC are 0.84, 0.88, and 0.94, respectively. These correlation coefficients are significant at, or greater than, the 99% confidence level. The error associated with the Nd and Yb measurements is <1% RSD and that for Gd is <5% RSD (see Section 4.2). The strongest correlation, however, is between DOC and pH (i.e., r=0.94), which reflects the substantial effect DOC has on pH in these low alkalinity and, hence, weakly buffered waters. It is important to note that because the pH and DOC of these waters cluster in two broad groups (e.g., pH~4.5 and 6.3; Fig. 3), the correlation coefficients are likely influenced by the bimodal spread of pH and DOC values.

The Skeeter Crossing sample was not considered in these statistical calculations for a number of reasons. This sample exhibits among the highest pH (6.4) and dissolved REE concentrations of those collected, but also has the lowest DOC concentration measured (Tables 1 and 2). The DOC concentration of the Skeeter Crossing sample (445 μmol/kg) is less than half the value of the next lowest measured DOC value (i.e., Cypress Swamp 2, DOC=952 μmol/kg), 22 times lower that the DOC concentration measured in Jericho Ditch water, and roughly 11 times lower than the mean DOC concentration of Lake Drummond waters. The higher pH and REE concentrations along with the relatively lower DOC value of the Skeeter Crossing sample is consistent with this water being groundwater or soil water (see Section 3). The higher pH may originate from chemical weathering reactions involving aquifer/soil materials, and the high REE concentrations may reflect large rock (or soil)/water ratios and relatively long residence times in the aquifer/soil materials compared to the surface waters studied.

Although DOC is lower in the Skeeter Crossing sample compared to the swamp waters, it is within the range reported for other natural terrestrial waters, including world average river water (~300–500 μmol C/kg; Degens, 1982). Tang and Johannesson (2003) suggested, based on model calculations (i.e., Humic Ion-Binding Model V; Tipping, 1994) that the concentration of DOC in world average river water at neutral pH was sufficient to complex all dissolved REEs. The CLE/ACSV measurements and the Model V predictions presented here (Figs. 5 and 6, respectively) indicate that the abundance of metal complexing (i.e., binding) sites associated with natural dissolved organic matter in Great Dismal Swamp waters exceeds the corresponding dissolved REE concentrations. Hence, DOC is not a limiting factor and appears to be sufficient to control the dissolved REEs concentrations in Great Dismal Swamp waters, including those of Skeeter Crossing.

Neodymium, Gd, and Yb are plotted in Fig. 7 versus distance along the studied flow system in a manner similar to that for pH and DOC shown in Fig. 2. Although we have not measured REE concen-

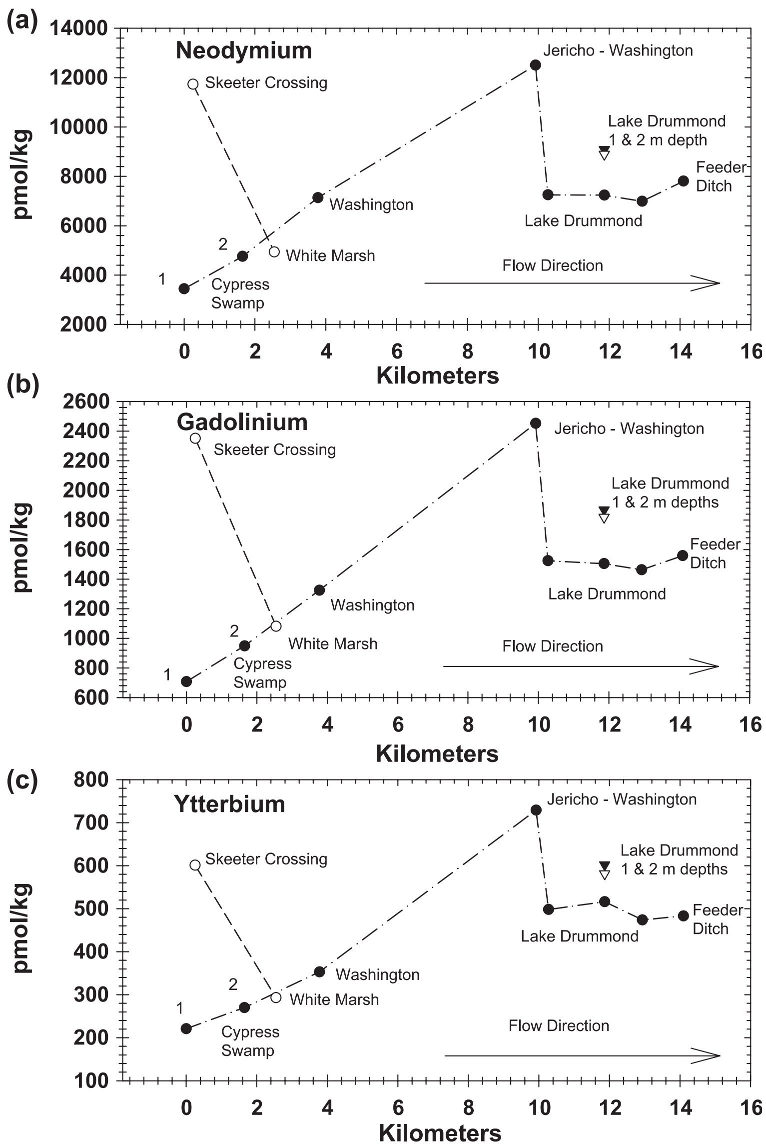

Fig. 7. Concentrations of Nd (a), Gd (b), and Yb (c) versus distance (in kilometers) along the general flow path of waters in the study region. Skeeter Crossing sample is thought to reflect groundwater (i.e., base flow), and thus is connected to the White Marsh sample, which is down stream from Skeeter Crossing (Fig. 1) by a dashed line. Otherwise, symbols are the same as in Fig. 2.

trations in Jericho Ditch water, the general patterns for individual REE concentrations versus distance are inverse to the pattern exhibited for pH versus distance. That is, as pH values decrease along the length of the flow system, the dissolved REE concentrations increase (Figs. 2 and 7). In addition, the relative distribution of REE concentrations along the flow direction also closely resembles the DOC concentrations in that as DOC concentrations increase, the REE concentrations also increase. As DOC concentrations likely control pH in these low alkalinity waters, the relationships shown in Figs. 2 and 7 strongly suggest that DOC also plays an important role in controlling REE concentrations in these natural waters. The speciation calculations and the CLE/ACSV measurements (Figs. 5 and 6) underscore the importance of DOC to REE concentrations in Great Dismal Swamp waters.

The results of the Humic Ion-Binding Model V calculations indicate that REEs chiefly exist as complexes with naturally occurring dissolved organic matter in waters of the Great Dismal Swamp (Fig. 6). Organic matter control of dissolved REE concentrations is supported by a number of other investigations. For example, McCarthy et al. (1998a) argued that natural organic matter facilitates REE, as well as actinide series element, transport in groundwater flow systems. Takahashi et al. (2002) demonstrated that Eu and the actinide Cm are strongly complexed by fulvic acid in circumneutral pH water. Furthermore, ultrafiltration studies have shown that REEs are commonly associated with natural organic matter in natural waters (e.g., Tanizaki et al., 1992; Viers et al., 1997; Dupré et al., 1999; Ingri et al., 2000). Tang and Johannesson (2003) illustrated that to a first approximation, Humic Ion-Binding Model V is able to reproduce the results of these earlier ultrafiltration studies. That is, both the ultrafiltration studies and the Model V predictions indicate strong relationships between REEs and organic matter in natural waters (see Tang and Johannesson, 2003). It is important to note that the terms "organic matter-bound REE solution complexes" and/or "organic complexes of the REEs" employed by Tang and Johannesson (2003) include REEs complexed to both low and high molecular weight natural organic matter (e.g., fulvic and humic acid fractions, respectively), as well as simple organic ligands (low molecular weight), which are considered dissolved and colloidal organic matter in other studies (Tanizaki et al., 1992; Viers et al., 1997; Ingri et al., 2000). Comparison of the results of the model calculations with the ultrafiltration studies indicates that Model V consistently performs better at predicting the complexation behavior of HREEs than LREEs with natural organic matter (Tang and Johannesson, 2003). Nevertheless, Model V does a reasonably good job reproducing the ultrafiltration results considering the many assumptions in the model.

The CLE/ACSV measurements suggest that the concentration of organic matter binding sites in filtered (0.45 μm) Washington Ditch waters are more than sufficient to complex all of the "dissolved" La before the binding sites are saturated with La. The suppression of the La signal (i.e., Fig. 5) clearly indicates La is strongly complexed with organic matter in Washington Ditch water. Although the CLE/ACSV results are only preliminary and work is currently ongoing to better refine the technique, the fact that they support the Model V predictions is compelling. It is important to note that Model V, as conceived, was designed to model speciation of metals with humic materials (Tipping and Hurley, 1992). Consequently, the model may not adequately account for metal complexation with other naturally occurring organic ligands, such as siderophores or phytochelatins, which are likely to be strong complexing ligands for REEs (e.g., Brantley et al., 2001; Ahner et al., 1997), and which may be reflected in the CLE/ACSV results but not the Model V predictions (Bruland et al., 1991; Xue and Sigg, 1999). Nonetheless, the correlation between dissolved REEs and DOC, the Model V predictions, and the results of the preliminary CLE/ASCV titrations are all consistent with complexation of REEs with organic ligands in Great Dismal Swamp waters and control of REE concentrations in these waters by dissolved organic matter (Figs. 2 and 7).

6.2. REE fractionation patterns

The MREE enriched fractionation patterns of Great Dismal Swamp waters (Fig. 4) are also compelling in that they are unusual among natural waters as a whole, but grossly similar to other acidic natural waters (e.g., Johannesson and Lyons, 1995; Gimeno et al., 2000). The origin of the MREE enriched fractionation patterns of Great Dismal Swamp waters is intriguing though because of the relatively high DOC concentrations of these waters compared to other natural waters exhibiting MREE enrichments. Unfortunately, our data are insufficient to conclusively establish the fractionation mechanism responsible for the MREE enrichments of Great Dismal Swamp waters. However, specific mechanisms have been advanced by other researchers to explain MREE enrichments in natural waters including weathering of MREE enriched phosphatic minerals/materials such as apatite/rhabdophane, dissolution/leaching of MREE enriched Fe–Mn oxides/oxyhydroxides, the presence of MREE enriched colloids, solution complexation, and degradation of natural organic matter. Any or all of these processes/sources may contribute to the development of the MREE enriched fractionation patterns of Great Dismal Swamp waters. Below we briefly examine each possibility.

Because of the low pH and high DOC that characterizes Great Dismal Swamp waters, it is conceivable that organic acids present in solution could contribute to apatite/rhabdophane dissolution, which may subsequently impart a MREE enriched signature to these waters (e.g., Hannigan and Sholkovitz, 2001; E.H. Oelkers, 2003, written comm.). Sediments and sedimentary rocks in the Great Dismal Swamp region consist chiefly of clastic materials shed off the Appalachian Mountains and the Piedmont region directly to the west (Mixon et al., 1989). These sedimentary materials may contain detrital apatite of igneous as well as biogenic origin, both of which may exhibit MREE enriched fractionation patterns (e.g., Wright et al., 1987; Grandjean et al., 1987; Grandjean-Lécuyer et al., 1993; Felitsyn et al., 1998a; Picard et al., 2002). Hannigan and Sholkovitz (2001) demonstrated that leaching of river sediments that showed no evidence of MREE enrichments compared to shale and phosphatic shales that were enriched in MREE, produced leachates enriched in the MREEs. Substantially greater MREE enrichments were reported when both substrates were leached with pH 2 compared to pH 5 solutions, strongly suggesting apatite dissolution as the source of the MREE enrichments of the leachates (Hannigan and Sholkovitz, 2001). These experiments, however, were not performed in the presence of high dissolved organic matter concentrations, and hence, the importance of natural organic acids cannot be ascertained.

It is well known that apatite exhibits low solubilities in waters of circumneutral pH (i.e., $K_{sp}=10^{-53}$; Taunton et al., 2000) such as those of Skeeter Crossing and the other waters from west of the Suffolk Scarp (pH 6.2–6.4; Table 1). However, apatite solubility increases dramatically with decreasing pH (Taunton et al., 2000) and consequently, dissolution of apatite or rhabdophane by the acidic Great Dismal Swamp waters could explain their characteristic MREE enrichments (Fig. 4). Great Dismal Swamp waters are all substantially undersaturated with respect to apatite (i.e., fluorapatite), and hydroxyapatite, with waters east of the Suffolk Scarp exhibiting greater degrees of undersaturation compared to waters to the west of the scarp. Using PHREEQC, for example, the saturation index, SI [where SI=log (IAP/K_{sp}), and IAP=ion activity product], for fluorapatite and hydroxyapatite in Cypress Swamp 1 waters (west of Suffolk Scarp) are −8.04 and −10.26, respectively, whereas for Lake Drummond the corresponding values are −25.5 and −27.1, respectively. Thus, equilibrium thermodynamics suggests that the organic acid-rich waters of the Great Dismal Swamp can dissolve apatite. It is important to note, however, that dissolved phosphorous concentrations in slightly acidic soil waters are commonly fixed by ubiquitous, and essentially insoluble, soil-zone Al and Fe phosphates (Taunton et al., 2000).

Solubility product data for REE-rich apatite and/or rhabdophane [i.e., $(Ce,La)PO_4 \cdot H_2O$] is necessary in order to critically evaluate solubility controls of these minerals on aqueous REE concentrations. However, to the best of our knowledge such data do not exist in the literature, although an ongoing investigation of REEs in equilibrium with apatite and rhabdophane is roughly consistent with our data (Fig. 3; E.H. Oelkers, 2003, written comm.). In the absence of appropriate REE-rich apatite/rhabdophane solubility product data, an alternative approach is to estimate activity products for individual REE phosphates (e.g., $LnPO_4 \cdot nH_2O$) and compare these to appropriate individual solubility products (e.g., Byrne and Kim, 1993; Johannesson et al., 1995). Calculated activity products for hypothetical Nd, Gd, and Yb phosphate coprecipitates in Great Dismal Swamp waters are plotted in Fig. 8 along with corresponding infinite dilution solubility product curves. The solubility product values for REE phosphate coprecipitates at zero ionic strength are those of Liu and Byrne (1997; dashed lines) and recalculated values from Firsching and Brune (1991; solid lines).

Fig. 8 indicates that waters from west of the Suffolk Scarp (e.g., Lake Drummond) are saturated with respect to Nd phosphate coprecipitates and undersaturated with respect to Gd and Yb phosphate coprecipitates, whereas waters from west of the scarp are oversaturated with respect to Nd, Gd, and Yb phosphate coprecipitates, but approach saturation for individual REEs as atomic number increases across

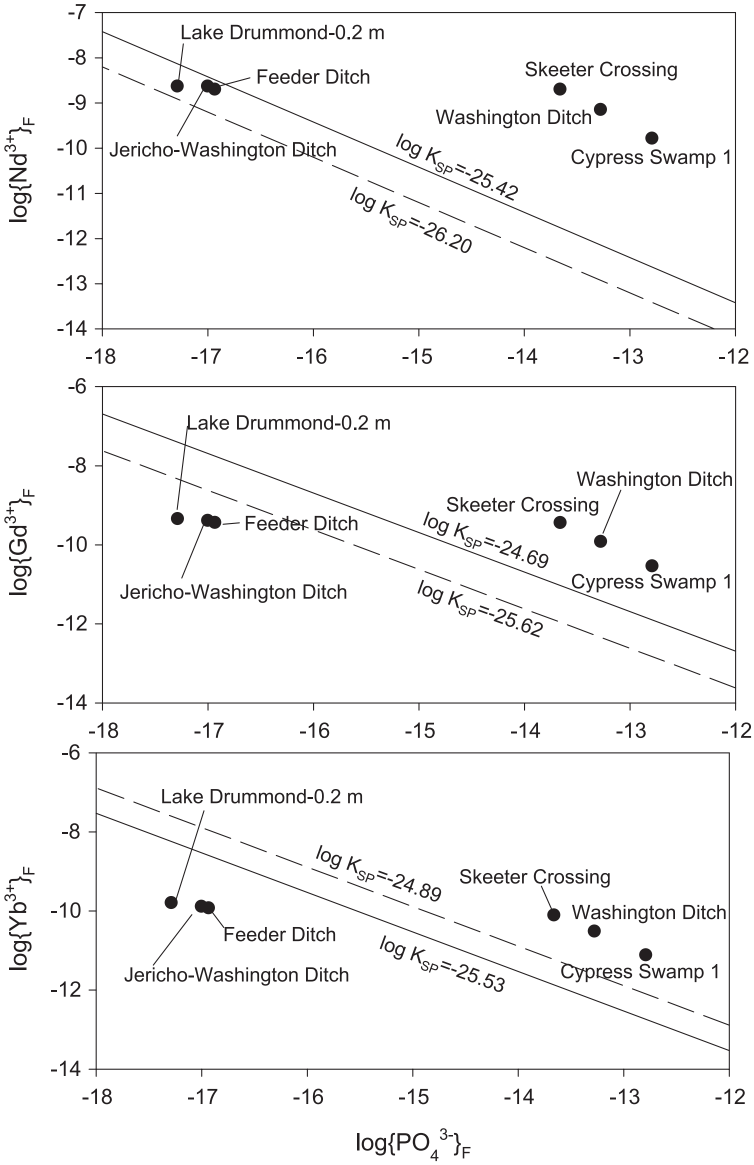

Fig. 8. Activities of free Nd^{3+}, Gd^{3+}, and Yb^{3+} versus free PO_4^{3-} as log quantities for waters from the Great Dismal Swamp. The solubility product curves for $LnPO_4 \cdot nH_2O$ at zero ionic strength recommended by Liu and Byrne (1997) are plotted as dashed lines for corresponding Ln^{3+} and PO_4^{3-} activities, whereas the values of Firsching and Brune (1991), recalculated to zero ionic strength, are shown as solid lines. The proximity of these waters to the solubility product curves suggest that they are, to a first approximation, roughly saturated with respect to REE phosphate coprecipitates (see text for discussion).

the REE series. Hence, REE phosphate coprecipitates could dissolve in the more acidic waters from east of the Suffolk Scarp, but not in the waters from west of the scarp where these phases should precipitate. Byrne et al. (1996) argued that in the absence of significant solution complexation (e.g., dilute, acidic waters), coprecipitation of REE phosphates will deplete aqueous solutions in MREEs relative to LREEs and HREEs. The fact that waters from west of the Suffolk Scarp are not depleted in MREE but are instead enriched (Fig. 4), suggests that complexation of REEs with natural organic ligands may play a role in enriching MREEs in waters. However, if MREE enriched phosphates coprecipitates exist in the Great Dismal Swamp substrate, then their dissolution by the acidic swamp waters east of the scarp could explain the observed MREE enrichments (Fig. 4). The outstanding feature of Fig. 8, however, is the striking similarity between the calculated activity products for Great Dismal Swamp waters and the solubility products, especially considering the uncertainties in these calculations, as well as the uncertainties associated with choosing the appropriate solubility products. Consequently, to a first approximation, Fig. 8 indicates that waters from the Great Dismal Swamp are roughly saturated with respect to REE phosphate coprecipitates (e.g., Byrne and Kim, 1993; Johannesson et al., 1995).

Chemical weathering (i.e., dissolution/leaching) of Fe–Mn oxides/oxyhydroxides contained within the local sedimentary deposits, including coatings of such materials on individual sediment grains, could also contribute to the formation of MREE enrichments in Great Dismal Swamp waters. Johannesson and Lyons (1995) suggested that MREE enrichments in the acidic waters of Colour Lake (Canadian High Arctic) could reflect dissolution/leaching of MREE enriched Fe–Mn oxides/oxyhydroxides. Johannesson and Zhou (1999) tested this hypothesis by leaching rocks of the Colour Lake watershed with a 0.04 M hydroxylamine hydrochloride (0.04 M $NH_2OH \cdot HCl$) solution in 25% (v/v) glacial acetic acid (CH_3COOH) to selectively dissolve Fe–Mn oxide/oxyhydroxide phases present in the rock samples. These authors concluded that the lake water's unique MREE enriched signature most likely reflected chemical weathering reactions involving dissolution of MREE enriched Fe–Mn oxides/oxyhydroxides by the acidic waters of the Colour Lake watershed. It is also possible that a similar process acts to generate the MREE enriched patterns of the Great Dismal Swamp waters. However, as in the case of apatite weathering, without REE data for Fe–Mn oxides/oxyhydroxides from the sediments and/or sedimentary rocks of coastal Virginia, it is impossible to assess the importance of these mineral/amorphous phases to the observed REE fractionation patterns of the local surface waters.

Some investigators have shown that colloidal fractions of REEs can exhibit MREE enrichments (Elderfield et al., 1990; Sholkovitz, 1995; Zhang et al., 1998; Ingri et al., 2000; Åström and Corin, 2003). Therefore, it is possible that the MREE enriched patterns of Great Dismal Swamp waters reflect a colloidal pool exhibiting such fractionation patterns. However, because we only filtered our samples though 0.45 μm pore-size filters, we cannot directly test this hypothesis. Future investigations will require ultrafiltration studies to adequately address the possibility of a colloidal origin of the MREE enrichments of Great Dismal Swamp waters.

In the case of organic-rich waters such as those of the Great Dismal Swamp, it is conceivable that the organic matter present in these waters and/or within the local swamp and lake sediments could contribute to the development of the MREE fractionation patterns of the waters. Other investigators have reported that MREEs are chiefly bound to organic matter in river sediments, and that the organic matter fraction of river water suspended loads typically exhibit MREE enrichments (Zhang et al., 1998; Leleyter et al., 1999). Fig. 9 is a plot of REE intrinsic binding constants (i.e., K_{MHA}) for type A sites of Model V (i.e., carboxyl sites; Tipping and Hurley, 1992) estimated by linear free-energy techniques for both humic and fulvic acids (Tang and Johannesson, 2003). These sites are thought to be essentially deprotonated at pH<7.0 (Tipping, 2002). Although the K_{MHA} values of Tang and Johannesson (2003) are only first approximations of the actual constants and are based on limited experimental data for three of the REEs (i.e., Eu, Tb, Dy) and other trace elements in the data base of Model V (e.g., Tipping and Hurley, 1992), they are intriguing in that MREEs (i.e., Sm, Eu) exhibit the greatest type A site intrinsic binding constants (i.e., K_{MHA}) to humic and fulvic acids, followed by the heaviest REEs (Tm, Yb, Lu; Fig. 9), and finally the LREEs. Because Model V predicts that organic matter complexes dominate REE speciation in Great Dismal Swamp waters, it is possible that these humic acid, and to a lesser degree, fulvic acid complexes may preferentially enrich MREEs in solution as a result of the greater intrinsic binding constants (i.e., K_{MHA}) of the MREEs relative to other REEs. Although highly speculative, the sim-

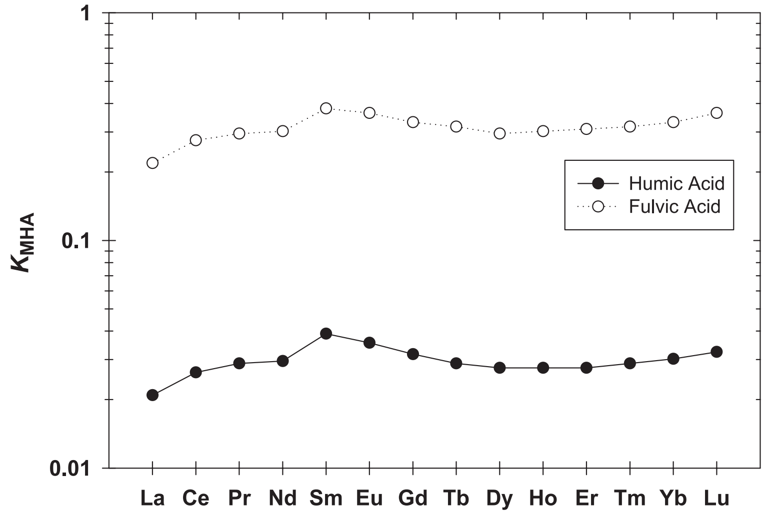

Fig. 9. Estimated K_{MHA} values for Humic Ion-Binding Model V determined by linear free-energy techniques as outlined in Tang and Johannesson (2003).

ilarities in the overall shape of the UCC-normalized REE patterns for Great Dismal Swamp waters and the pK_{MHA} values estimated by Tang and Johannesson (2003), including the greater normalized values for the HREEs compared to the LREEs (Figs. 4 and 9), is compelling.

Finally, recent investigations of REE concentrations of humic acids indicate enrichments in MREE when normalized to a shale composite (Felitsyn et al., 1998b; Felitsyn and Morad, 2002). Indeed, the shale-normalized REE patterns of Eocene humics presented by Felitsyn and Morad (2002) closely resemble the UCC-normalized REE patterns of Great Dismal Swamp waters. The Eocene humic acid extracted and analyzed by Felitsyn and Morad (2002) exhibits MREE enrichments similar to those for Great Dismal Swamp waters, having lower shale-normalized LREE values compared to the normalized HREE values that also closely resemble the fractionation patterns of Great Dismal Swamp waters (Fig. 4). Consequently, it is conceivable that degradation/decomposition and solubilization of MREE enriched organic materials (i.e., humics) in sediments within the Great Dismal Swamp watershed is the direct source of the fractionation patterns exhibited by REEs in the local waters. This is consistent with the relatively strong and significant correlation between REE and DOC concentrations in waters of the watershed, and the predicted dominance of organic matter complexes of REEs in these waters.

7. Conclusions

Rare earth element concentrations of the moderately acidic waters of the Great Dismal Swamp watershed of southeastern Virginia are higher than circumneutral pH waters, but similar to other low pH natural waters. Aqueous REE concentrations are inversely correlated to pH, but directly correlated to DOC concentrations. The correlations of REEs with DOC increase with increasing atomic number across the REE series, and are overall stronger between REEs and DOC than REEs and pH. Application of Humic Ion-Binding Model V to REE speciation in Great Dismal Swamp waters predicts that organic matter complexes dominate REE speciation in these waters. Competitive ligand equilibration adsorptive cathodic stripping voltammetric titrations of Great Dismal Swamp water samples are consistent with dominance of organic matter complexation of REEs. Together, the correlations, Model V predictions, and the voltammetric analyses are strong evidence that natural organic ligands exert important controls on REE concentrations in certain natural waters.

Acknowledgments

This project was funded by NSF Grant EAR-0001086 to K.H. Johannesson and J.R. Donat. We are also grateful to the Department of Ocean, Earth, and Atmospheric Sciences at Old Dominion University for providing partial support for J. Tang and the Department of Geology at The University of Texas at Arlington for providing office space for J. Tang. We thank H. Reeves for help during sample collection, N. McGinnis for assistance with data processing, and D. Miller for drafting the map of the study region. We are especially grateful to J.R. Donat for his invaluable assistance with the voltammetric titrations, and for use of his laboratory facilities. **[EO]**

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