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ORIGINAL PAPER

Arsenic Geochemistry of the Great Dismal Swamp, Virginia, USA: Possible Organic Matter Controls

Shama E. Haque · Jianwu Tang · William J. Bounds · David J. Burdige · Karen H. Johannesson

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Abstract Surface water samples for arsenic (As) concentration and speciation analysis were collected from organic matter-rich blackwaters of the Lake Drummond portion of the Great Dismal Swamp in southeastern Virginia, USA. Arsenic concentrations and speciation were determined by selective hydride generation, gas chromatography with photoionization detection. Surface waters from the Great Dismal Swamp are high in dissolved organic carbon (DOC) concentrations (445–9,600 μmol/kg) and of low pH (4.2–6.4). Total dissolved As concentrations [i.e., As(III) + As(V)], hereafter As_T, range from 2.2 nmol/kg to 21.4 nmol/kg. Arsenite, As(III), concentrations range from ~ 1 nmol/kg to 17.7 nmol/kg, and As(V) ranges from ~ 1 nmol/kg to 14.1 nmol/kg. Arsenate, As(V), is the predominant form of dissolved As in the inflow waters to the Great Dismal Swamp, whereas within the swamp proper arsenite, As(III), dominates. Arsenite accounts for 8–37% of As_T in inflow waters west of the Suffolk Scarp, and between 54% and 81% of As_T in Lake Drummond and Great Dismal Swamp waters east of the scarp. Arsenite is strongly correlated to DOC ($r = 0.94$) and inversely related to pH ($r = -0.9$), both at greater than the 99% confidence level. Arsenate is weakly related to pH and DOC ($r = 0.4$ and -0.37, respectively), and neither relationship is statistically significant. No statistical relationships exist between As(V) or As(III) and PO_4 concentrations. The predominance of As(III) and its strong correlation with DOC in Great Dismal Swamp waters suggest that

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S. E. Haque
Department of Earth and Environmental Sciences, The University of Texas at Arlington,
Arlington, TX 76019-0049, USA

J. Tang
Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12,
Graz 8010, Austria

W. J. Bounds · D. J. Burdige
Department of Ocean, Earth, and Atmospheric Sciences, Old Dominion University,
Norfolk, VA 23529-0276, USA

K. H. Johannesson (✉)
Department of Earth and Environmental Sciences, Tulane University, New Orleans,
LA 70118-5698, USA
e-mail: kjohanne@tulane.edu

DOC may inhibit As(III) adsorption or form stable aqueous complexes with As(III) in these waters. Alternatively, phytoplankton and/or bacterially mediated reduction of As(V) may be important processes in the organic-rich blackwaters and/or sediment porewaters of the swamp, leading to the prevalence of As(III) in the water column.

Keywords Arsenic · Chemical speciation · Organic matter · Great Dismal Swamp · Northwest River

1 Introduction

Arsenic (As) is known to detrimentally affect human health in a variety of ways including cardiovascular, respiratory, and neurological diseases, and is regarded as the chief environmental cause of cancer deaths worldwide (e.g., National Research Council 1999; Schreiber et al. 2000; Nriagu 2002). Despite the existence and serious nature of anthropogenic sources of As, the primary cause of As poisoning to humans occurs via chronic exposure to elevated As in drinking water. Numerous well-documented cases of As poisoning from drinking water sources have been reported from across the globe including Vietnam, Ghana, Mexico, Chile, Argentina, eastern Europe, portions of the USA, as well as Bangladesh and West Bengal, India (Smedley and Kinniburgh 2002). Although high dissolved As concentrations in drinking waters are a necessary concern, As toxicity to organisms, including humans, is primarily controlled by its chemical speciation rather than its total concentration. Consequently, to quantitatively understand As behavior and cycling in natural waters, it is not enough to only measure total dissolved concentrations as speciation data are also critical.

Arsenic can occur in multiple oxidation states in natural waters including As(–III), As(III), and As(V) in addition to methylated forms (e.g., monomethyl, MMA, and dimethyl arsenic, DMA) and other organoarsenicals. In oxygenated waters, equilibrium thermodynamics predicts that arsenate [As(V)] will predominate as $H_2AsO_4^- + HAsO_4^{2-}$, whereas under reducing conditions, arsenite [As(III) as $H_3AsO_3^0$] will dominate (Cullen and Reimer 1989). However, both arsenate and arsenite can persist in reducing and oxidizing conditions, respectively, indicating that the rates of oxidation/reduction of these species are slow and/or that biological process likely contribute to As species disequilibrium (Ferguson and Garvis 1972; Cutter 1992; Sanders and Riedel 1993; Oremland and Stolz 2003). Although investigation of the rates of oxidation and reduction of As species under environmentally relevant conditions will facilitate an improved understanding of As redox cycling (Inskeep et al. 2002), the specifics concerning biological cycling of As species are complex (e.g., Stolz and Oremland 1999; Oremland and Stoltz 2003, 2005; Oremland et al. 2005). In surface waters, for example, biotic processing of As at the first trophic level primarily involves uptake of As(V) by phytoplankton, owing to its chemical similarity to phosphate, followed by its in vivo conversion to methylated forms and/or As(III) as a means of detoxification, and subsequent expulsion from the cell into the water column (Andreae and Klumpp 1979; Sanders 1979; Wrench et al. 1979; Sanders and Windom 1980; Maeda et al. 1990a, b; Sanders and Riedel 1993; Hellweger et al. 2003; Hellweger and Lall 2004). Consequently, biotransformation of As(V) by phytoplankton can augment As(III) concentrations in surface waters (e.g., Aurilio et al. 1994; Sohrin et al. 1997; Hellweger et al. 2003). Moreover, bacterially mediated As reduction and oxidation (e.g., Oremland et al. 2000, 2005) can promote As species disequilibrium in natural waters. Finally, solution and surface complexation reactions involving dissolved As species with aqueous or surface ligands may stabilize As species in environments that thermodynamics would not predict as stable (Redman et al. 2002).

In this contribution, we present As concentration and speciation data for waters from the Great Dismal Swamp in southeastern Virginia along with pH, dissolved organic carbon (DOC), and phosphate concentrations in order to investigate potential relationships between dissolved As species and these biogeochemical parameters. Recent laboratory experiments (Kalbitz and Wennrich 1998; Redman et al. 2002; Simeoni et al. 2003; Dobran and Zagury 2005) demonstrate that natural organic matter (NOM) can enhance As mobility in the environment, especially in the case of arsenite, As(III). Statistical analysis is employed to evaluate the significance of DOC, phosphate, and pH on As(III) and As(V) concentrations in waters of the Great Dismal Swamp. To the best of our knowledge, the As speciation data presented here for Great Dismal Swamp waters are the first such data for a blackwater system from the southeastern USA. Despite numerous studies of Hg in wetlands environments of the southeastern USA (e.g., Hurley et al. 1998; Cleckner et al. 1999), little effort has focused on the investigation of As in these systems.

2 Study Area

The Great Dismal Swamp is located on the coastal plain of southeastern Virginia and northeastern North Carolina between the drainage basins of the James River to the north and Albemarle Sound to the south (Fig. 1). The swamp is flanked on the west by the Suffolk Scarp, a north trending, linear structure proposed to be a paleo-marine shoreline (Fig. 1; Oaks and Whithead 1979). The eastern boundary is more diffuse, converging with the numerous tidal creeks and waterways that delineate Virginia's and North Carolina's "tidewater" region. The swamp currently occupies an area of about 1,800 km^2. Our study focuses on Lake Drummond (and its watershed), which is a shallow ($\sim$2 m deep), well-mixed blackwater lake located in the northern, Virginia section of the swamp (Fig. 1). Lake Drummond has a surface area of $\sim$13 km^2, and the upland region west of the lake, which drains into the lake and comprises the lake's watershed, occupies nearly 98 km^2 (Lichtler and Walker 1979; Marshall 1979). The Cypress Swamp–Washington Ditch flow system is one of the principal surface water inflows to Lake Drummond (Fig. 1). The East Ditch also contributes significant surface water inflows to the lake (Lichtler and Walker 1979). The chief surface water outflow from Lake Drummond occurs via the Feeder Ditch. The Feeder Ditch subsequently discharges into the Dismal Swamp Canal (part of the Intercoastal Waterway) and the Northwest River, a major drinking water source for the City of Chesapeake, Virginia (Fig. 1; Lichtler and Walker 1979). The Northwest River drains to the Currituck Sound and Albemarle Sound, both within North Carolina (See Oaks and Whitehead 1979).

Mean annual precipitation at Lake Drummond is 1,280 mm, and the mean annual temperature in the region varies between 15°C and 15.4°C (Lichtler and Walker 1979). Potential inflow to the swamp from the upland regions to the west is as much as 321.4×10^3 m^3/day, although only 135.8×10^3 m^3/day of this total is estimated to recharge Lake Drummond as the remainder (185.6×10^3 m^3/day) is captured and drained by the numerous ditches constructed within the swamp (Lichtler and Walker 1979).

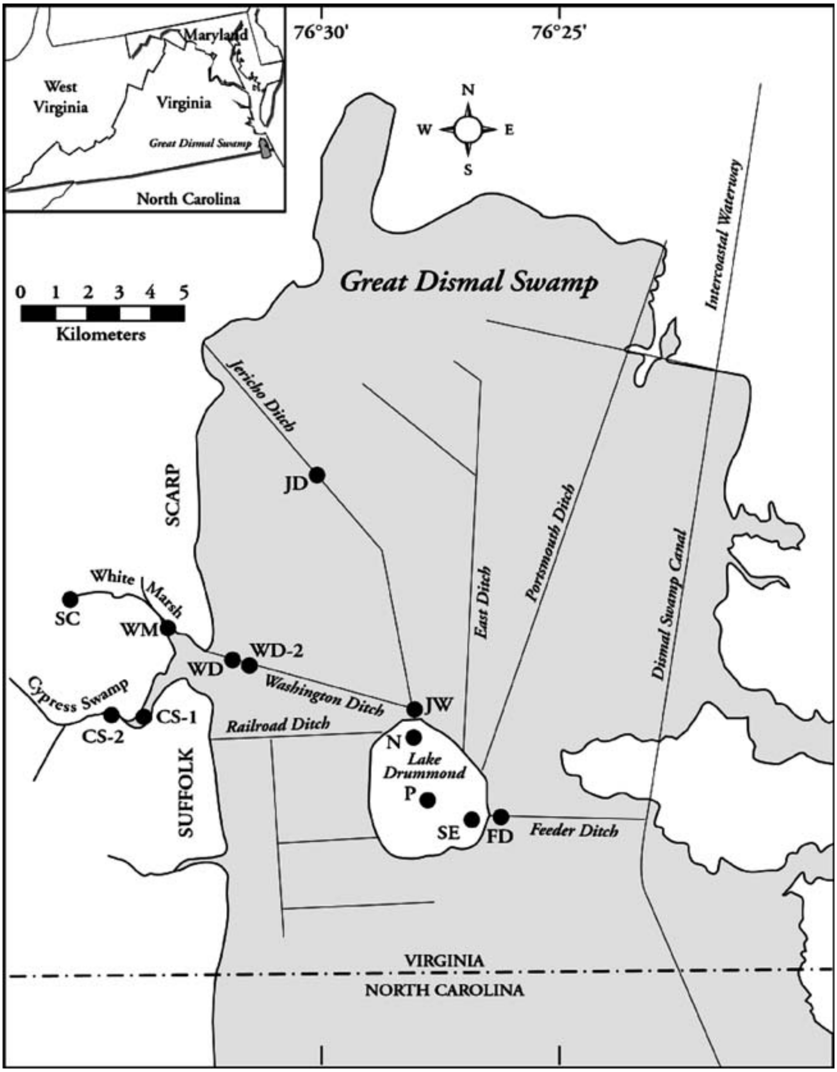

Fig. 1 Map of the study region within the Virginia portion of the Great Dismal Swamp centered on Lake Drummond. Sample locations are indicated by filled circles and the following labels: SC = Skeeter Crossing; WM = White Marsh, CS-2 = Cypress Swamp 2; CS-1 = Cypress Swamp 1; WD = Washington Ditch; WD-2 = Washington Ditch 2 (not sampled in this study); JD = Jericho Ditch; JW = Jericho-Washington Ditch; N = Lake Drummond North, P = Lake Drummond Profile, SE = Lake Drummond Southeast; FD = Feeder Ditch. Map is from Johannesson et al. 2004

3 Methods

3.1 Sample Collection

Prior to sample collection, all sample bottles were rigorously cleaned using trace element clean procedures (e.g., Johannesson et al. 2004). Surface water samples and one groundwater sample (i.e., Skeeter Crossing) were collected from Lake Drummond and its inflow and outflow streams/ditches within the Great Dismal Swamp watershed (Fig. 1). Because sampling for the study was limited to early summer (i.e., early July 2001), the data presented here cannot provide insights into seasonal variations in, or confirm biological controls on, As concentrations and speciation within the swamp waters. Nevertheless, our data set is the first to provide As concentration and speciation data for waters of the Great Dismal Swamp and surrounding environment, and hence is of particular importance to the city of Chesapeake, Virginia, which draws drinking water from sources originating in the Great Dismal Swamp.

Water samples were collected by pumping water through previously cleaned Teflon® tubing using a peristaltic pump, and subsequently through in-line filter capsules (Gelman Sciences, 0.45 μm, polyether sulfone membrane) attached to the tubing. Each pre-cleaned HDPE sample bottle was triple rinsed with the filtered water sample before the bottle was filled with the actual sample. The samples for As speciation measurements (1 l) were immediately double bagged, placed within an ice-chest filled with ice, and returned to the laboratory for analysis. Water samples were also collected to quantify dissolved NOM by analysis of the DOC content. These samples were filtered as above, collected in pre-cleaned glass vials, and immediately returned to the laboratory for analysis. Samples for major cations and anions were collected identically, except that the cation samples were preserved with a drop of ultra-pure HNO_3 (Seastar Chemicals; Welch et al. 1996; Johannesson et al. 2004).

Surface water samples from Lake Drummond, the Feeder Ditch, and the Jericho-Washington Ditch were collected from a small aluminum john-boat while motoring slowly into the wind, in the case of the lake, or upstream in each ditch sampled. The intake of the Teflon® collection tube was held well out in front of the vessel. The Jericho-Washington Ditch sample was collected downstream of the confluence of the Jericho and Washington Ditches, and approximately 100 m upstream from where the combined ditch (i.e., Jericho-Washington) flows into Lake Drummond (Fig. 1). The other chief inflow to Lake Drummond, the East Ditch (Fig. 1; Lichtler and Walker 1979), was inaccessible from the lake via the john-boat during our sampling excursion (early July 2001). All other samples, except the Skeeter Crossing sample, were collected from shore by placing the collection end of the Teflon® tube into the surface water body. 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 excavation, a water sample was collected as described above. Therefore, the Skeeter Crossing sample represents base flow (i.e., groundwater) in this small stream.

3.2 Sample Analysis

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 methods. Major cations and anions were determined in each water sample by ion chromatography (Dionex DX-500) following standard methods (e.g., Welch et al. 1996). The major anions (i.e., 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^+) were measured with Ion Pac CS12A and CG12A columns, a CSRS-ULTRA (4 mm) self-regenerating cation suppressor, and 20 mM methane sulfonic acid 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 NOM was examined by measuring the DOC concentrations of Great Dismal Swamp waters using high temperature catalytic oxidation (Shimazdu TOC-5000 total carbon analyzer; Burdige and Gardner 1998).

Determinations of As(III) and As(III + V) were made within 24 h of collection (L. S. Cutter, analyst) utilizing the selective hydride generation, gas chromatography with photoionization detection (GC/PID) method of Cutter et al. (1991). The method employs routine hydride generation techniques to speciate As, liquid nitrogen cold trapping of evolved arsine gases followed by slow warming gas chromatographic separation of the arsines (Andreae 1977, 1978, 1979; Andreae et al. 1981), and detection by photoionization (Vien and Fry 1988; Cutter et al. 1991). Briefly, the filtered water sample is added to a glass-stripping vessel and pH is then adjusted to 6.2 with 2.5 M Tris–HCl (Cutter et al. 1991; Cutter 1991). Then, 1.2 ml of a 4% $NaBH_4$ solution is added to the sample to produce arsine from As(III), which is subsequently collected on a liquid nitrogen cooled Pyrex® glass U-tube packed with dimethyldichlorosilane treated glass wool (Andreae 1977; Cutter et al. 1991). Following trapping of the arsines, the U-tube is removed from the liquid nitrogen, at which point the various hydrides are revolatilized and separated on a 4-m Carbopack B-HT 100 column (Supelco), and measured by a photoionization detector (10.2 eV lamp, HNU Systems; Cutter 1991; Cutter et al. 1991). The method has been employed successfully in studies of As species in seawater (Cutter 1991; Cutter and Cutter 1995; Cutter et al. 2001).

Analytical precision for the method is 3% relative standard deviation (RSD) for both As(III) and As(III + V) at low concentrations (i.e., 0.03 nmol of As/l), and 0.5% RSD at higher concentrations (1.9 nmol of As/l; Cutter et al. 1991). The method detection limit determined by Cutter et al. (1991) for a 50 ml sample was 11 pmol of As/l based on 3σ of the blank measurement. For the Great Dismal Swamp samples, analytical precision for both As(III) and As(III + V) was better than 5% RSD at concentrations >0.5 nmol of As/l (all samples; Table 1), and the method detection limit (3σ) for As(III) and As(III + V) was 1.0 pmol of As/l for the 1 l samples. Measurements for As(III) and As(III + V) were made in triplicate, and the mean (±standard deviation) of the triplicate measurements are presented in Table 1. Arsenate concentrations were subsequently calculated by difference from the mean As(III) and As(III + V) concentrations.

Determinations of monomethyl arsenic (MMA) and dimethyl arsenic (DMA) use the methods described by Andreae (1983a), modified for simultaneous detection using the inorganic As and Sb GC/PID system (Cutter et al. 1991), except that a 4 m 15% OV-3 on Chromosorb W/AW DMCS (80/100 mesh) column is employed to separate the methyl hydrides. These hydrides are quantitatively generated using the As(III + V) conditions (Andreae 1983a), with a detection limit of 5 pmol/l, and precision of 6% (RSD) at 0.1 nmol/l. It is important to note, however, that organoarsenicals were not detected in the Great Dismal Swamp samples likely owing to low concentrations combined with the limited size samples collected (i.e., 1 l).

4 Results

4.1 General Water Chemistry

Major solute concentrations of Great Dismal Swamp waters are presented in Table 1 along with the corresponding pH, temperature, PO_4, and DOC concentrations. Our major solute

Table 1 Dissolved solute composition, including arsenic speciation, of surface waters from the Great Dismal Swamp, southeastern Virginia, USA

	Cypress Swamp 1	Cypress Swamp 2	Skeeter Crossing	White Marsh	Washington Ditch	Jericho-Washington	Lake Drummond Southeast	Lake Drummond "P"	Lake Drummond North	Feeder Ditch
Ca	0.227	0.220	0.464	0.136	0.144	0.141	0.110	0.116	0.111	0.108
Mg	0.081	0.077	0.196	0.060	0.063	0.043	0.039	0.041	0.040	0.038
Na	0.190	0.188	0.204	0.225	0.224	0.193	0.183	0.183	0.181	0.177
K	0.075	0.073	0.138	0.064	0.065	0.043	0.042	0.042	0.041	0.041
Cl	0.267	0.257	0.799	0.284	0.283	0.247	0.250	0.253	0.249	0.249
Alk[a]	0.360	0.136	0.176	0.168	0.172	0.104	0.080	0.088	0.064	0.064
SO_4	0.178	0.184	0.270	0.110	0.135	0.039	0.045	0.045	0.043	0.044
NO_3	0.029	0.032	0.287	0.017	0.011	0.008	0.012	0.015	0.015	0.016
F	0.005	0.007	0.011	0.003	0.003	0.001	0.002	0.001	0.001	0.001
PO_4^b	1.06	1.21	0.18	0.52	NM	1.41	0.42	0.42	1.41	0.92
Arsenic species in surface waters (nmol/l ± SD)[c,d]										
As(III)	0.998 ± 2.74	4.79 ± 0.40	1.25 ± 0.02	7.09 ± 0.21	1.4	17.72 ± 0.64	9.99 ± 0.30	12.16 ± 0.10	12.78 ± 0.39	11.81 ± 0.02
As(V)	11.40	8.18	0.93	14.10	6.40	3.42	8.57	3.40	5.58	4.73
As(III + V)	12.35 ± 0.59	12.97 ± 2.36	2.18 ± 0.02	21.22 ± 0.64	7.8	21.42 ± 0.02	18.56 ± 0.30	15.56 ± 0.27	18.36 ± 0.55	16.54 ± 0.17
DOC[b]	1031	952	445	1040	1030	6304	4463	4442	4500	5109
pH	6.42	6.28	6.4	6.32	6.18	4.22	4.3	4.31	4.33	4.31
Temp (°C)	24.2	24.4	19.5	24.9	22.37	21.5	28.5	27.6	28.6	28.5

[a] as HCO_3

[b] in µmol/kg

[c] All determinations in triplicate

[d] SD = standard deviation

NM = not measured

Major solutes are in mmol/kg, dissolved organic carbon (DOC) and PO_4 concentrations are in µmol/kg, and arsenic species are in nmol/kg concentration data for Great Dismal Swamp waters are in close agreement with those of Lichtler and Walker (1979). 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). In addition, Great Dismal Swamp waters are all acidic, with pH ranging between 4.2 and 6.4. Waters that drain regions west of the Suffolk Scarp (i.e., Skeeter Crossing, White Marsh, Cypress Swamp 1 and 2, Washington Ditch), and which comprise inflow waters to Lake Drummond, are less acidic (by ~2 pH units) than waters east of the Suffolk Scarp (i.e., Jericho-Washington Ditch, Lake Drummond, Feeder Ditch; Fig. 2).

Great Dismal Swamp waters exhibit high DOC concentrations (Fig. 2; Table 1) that range from 445 μmol/kg in the Skeeter Crossing sample to 9,600 μmol/kg in the Jericho Ditch (i.e., site JD on Fig. 1; see Johannesson et al. 2004). Waters from west of the Suffolk Scarp have substantially lower DOC concentrations than waters from east of the scarp (Fig. 2; Table 1). 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 waters from east of the Suffolk Scarp is 5,563 ± 1,741 μmol/kg, or more than a factor of 6 greater than in the inflow waters. Dissolved organic carbon concentrations are inversely correlated to pH in Great Dismal Swamp waters ($r = -0.94$; Johannesson et al. 2004).

Future investigation may involve characterization of the dissolved NOM of Great Dismal Swamp water (e.g., fraction of NOM that is humic and fulvic acids, hydrophilic acids, and simpler organic compounds such as carbohydrates, amino acids, hydrocarbons; Thurman 1985). Although we did not characterize Great Dismal Swamp NOM as part of this study, it is reasonable to expect that its composition is grossly similar to NOM from other blackwater systems from the southeastern USA (e.g., Suwannee River, Okefenokee Swamp; Lobartini et al. 1991; Redman et al. 2002). Humic matter isolated from blackwater swamps and rivers from the Georgia Coastal Plain (i.e., Okefenokee Swamp, Satilla River, Ohoopee River), for example, consisted of, on average, 60–72% fulvic acid and 28–40% humic acid (Lobartini et al. 1991). Blackwater systems from the Georgia Coastal Plain also exhibit similar pH (3.8–6.2) and DOC concentrations (1,108–2,092 μmol/kg) to Great Dismal Swamp waters (Lobartini et al. 1991). However, it should be noted that the Great Dismal Swamp has DOC concentrations that are approximately a factor of 2 greater than values reported for the Okefenokee Swamp.

Other than the Skeeter Crossing groundwater sample, which exhibits a Cl concentration of 0.8 mmol/kg, Cl concentrations are uniform in Great Dismal Swamp waters (mean ± standard deviation = 0.26 ± 0.01 mmol/kg; Fig. 2). Orthophosphate concentrations are more variable in Great Dismal Swamp waters, ranging from 0.18 μmol/kg for the Skeeter Crossing groundwater sample, to 1.41 μmol/kg in the Jericho-Washington Ditch and the Lake Drummond sample closest to the inflow of this ditch (Fig. 2).

4.2 Arsenic Concentrations and Speciation

Arsenic concentrations and speciation results are presented in Table 1 and Fig. 3. Total As [i.e., As(III) + As(V), hereafter referred to as As_T] concentrations in Great Dismal Swamp waters range from 2.2 nmol/kg in the Skeeter Crossing groundwater sample up to 21.4 nmol/kg in the Jericho-Washington Ditch sample, and exhibit a mean (±standard deviation) of 14.7 ± 6.1 nmol/kg. (Arsenic samples were not collected from the Jericho Ditch site during the study.) On average, As_T concentrations are greater in waters from east

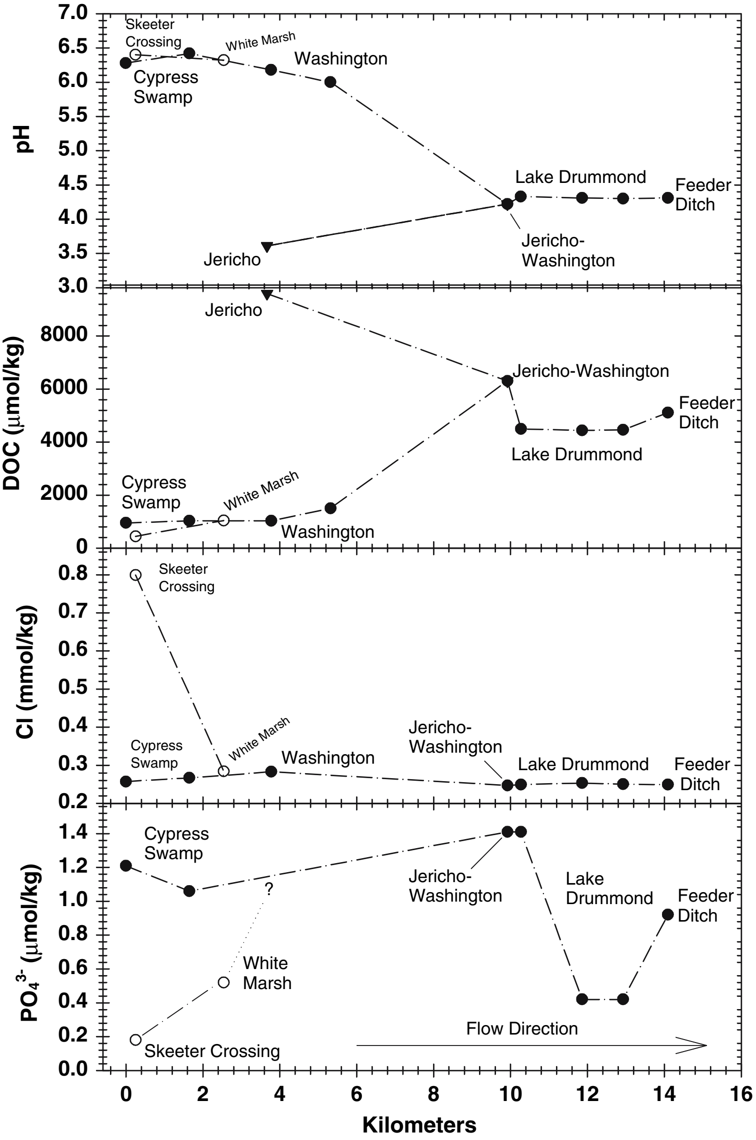

Fig. 2 Variation in pH, DOC, Cl, and PO_4 concentrations along the general flow path (in kilometers) of surface waters in the Lake Drummond portion of the Great Dismal Swamp. The Jericho Ditch sample represents waters that are not directly part of the White Marsh–Cypress Swamp inflow system. In addition, because the Skeeter Crossing and White Marsh samples are from a separate tributary to the Cypress Swamp (see Fig. 1), they are separated out of the Cypress Swamp samples using open circle symbols

of the Suffolk Scarp [Lake Drummond, Jericho-Washington Ditch, Feeder Ditch; mean As_T (±standard deviation) = 18.1 ± 2.2 nmol/kg] compared to the inflow waters west of the scarp [mean As_T (±standard deviation) = 11.2 ± 7 nmol/kg; Fig. 3].

Arsenite [i.e., As(III)] concentrations in Great Dismal Swamp waters range from ~1 nmol/kg in the Cypress Swamp 1 sample to 17.7 nmol/kg in water from the

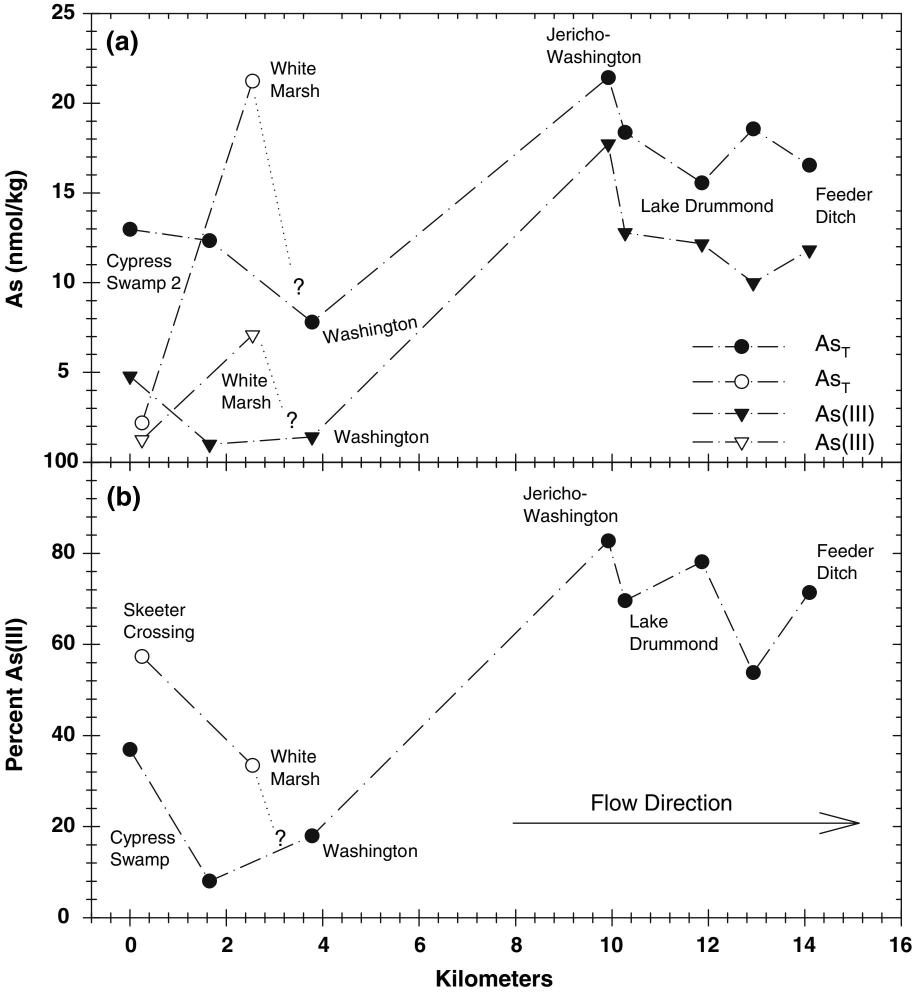

Fig. 3 Variation in (**a**) total dissolved arsenic, As_T [i.e., circles] and As(III) [inverted triangles] concentrations, and (**b**) percent of total dissolved arsenic that is As(III) along the general flow path (in kilometers) of surface waters in the Lake Drummond portion of the Great Dismal Swamp

Jericho-Washington Ditch (Table 1). Arsenate [i.e., As(V)] concentrations (i.e., calculated by difference; Andreae 1977; Cutter et al. 1991) range from 0.9 nmol/kg in the Skeeter Crossing groundwater sample to 14.1 nmol/kg in the White Marsh sample (Table 1). Arsenite predominates in all waters from east of the Suffolk Scarp, and hence, waters from within the Great Dismal Swamp proper, whereas As(V) dominates in the inflow waters west of the scarp (Table 1; Fig. 3). The only exception to this is the Skeeter Crossing groundwater sample for which 57% of As_T is As(III).

Both As_T and As(III) are positively correlated with DOC in Great Dismal Swamp waters, whereas As(V) exhibits a weak negative correlation with DOC (Fig. 4). The correlation coefficients for As_T, As(III), and As(V) versus DOC are 0.66, 0.94, and –0.37, respectively. Arsenite is most strongly correlated with DOC as indicated by its high

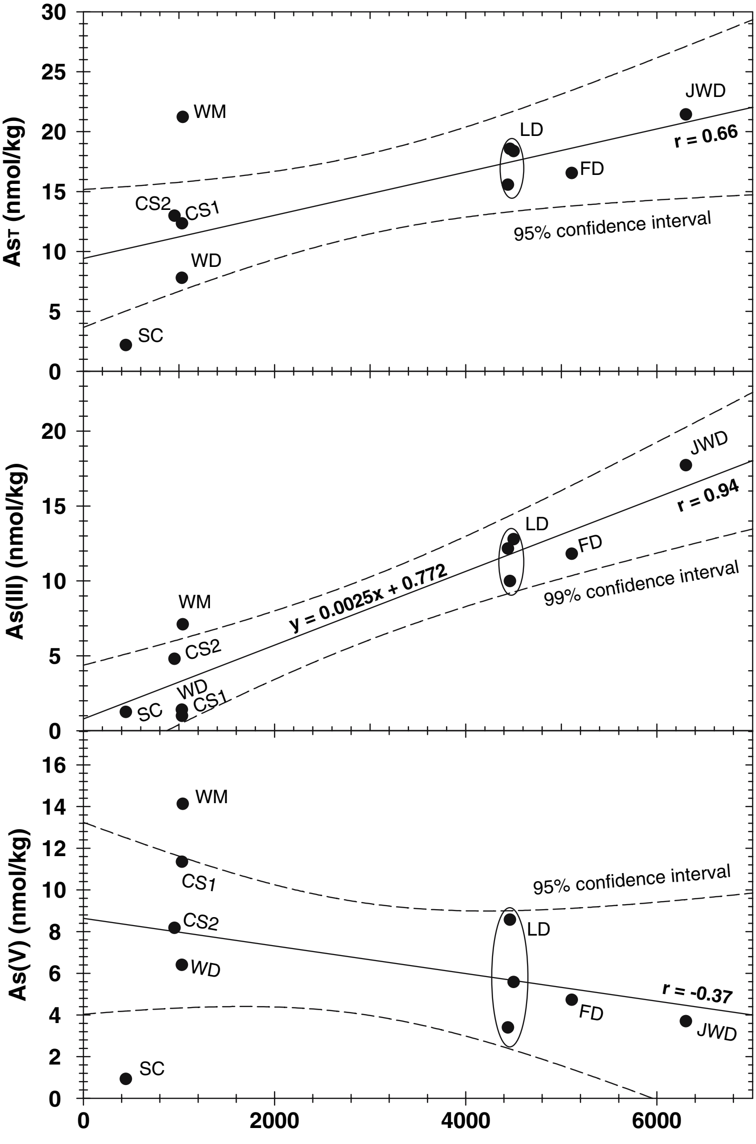

Fig. 4 Total dissolved arsenic, As_T, As(III), and As(V) concentrations versus DOC concentrations in Great Dismal Swamp waters. Linear regression curves, correlation coefficients, and confidence intervals are shown for each panel. Note, confidence intervals for As_T and As(V) are 95%, whereas for As(III) they are 99%. Samples are identified as in Fig. 1, except the Jericho-Washington Ditch sample is JWD. Linear regression curve for As(III) versus DOC is given as $y = 0.0025x + 0.772$

correlation coefficient, which is significant at greater than the 99% confidence level (Fig. 4). The moderate, positive correlation between As_T and DOC is significant at the 95% confidence level, whereas the weak, negative relationship between As(V) and DOC is not statistically significant.

Arsenite exhibits a strong negative correlation with pH ($r = -0.9$) that is significant at greater than the 99% confidence level (Fig. 5). Total dissolved As (i.e., As_T) shows a moderate inverse correlation with pH ($r = -0.6$) that is significant at less than the 90% confidence level. However, As(V) is only weakly correlated to pH ($r = 0.4$), and the

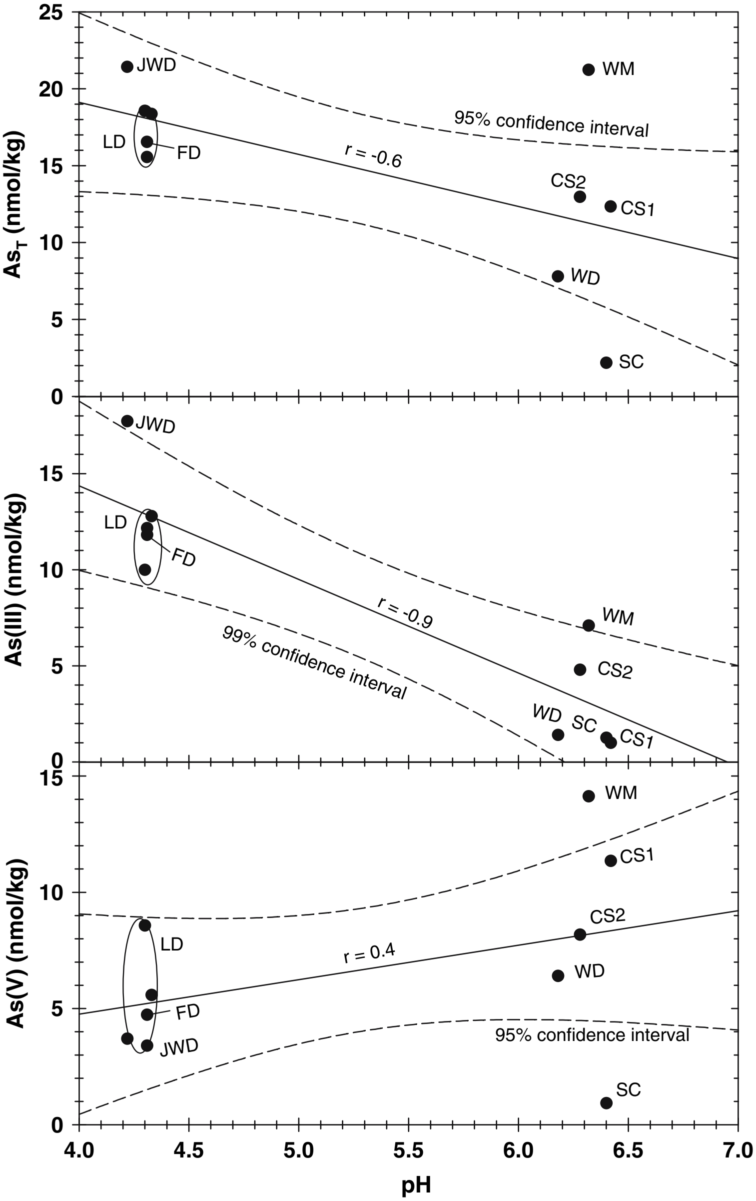

Fig. 5 Total dissolved arsenic, As_T, As(III), and As(V) concentrations versus pH in Great Dismal Swamp waters. Linear regression curves, correlation coefficients, and confidence intervals are shown for each panel. Note, confidence intervals for As_T and As(V) are 95%, whereas for As(III) they are 99%. Symbols identical to Fig. 4

correlation is not statistically significant (Fig. 5). None of the arsenic species exhibit statistically significant correlations with orthophosphate in Great Dismal Swamp waters. Correlation coefficients for As_T, As(III), and As(V) versus PO_4 are 0.41, 0.38, and 0.07, respectively.

5 Discussion

5.1 Geochemical Characterization of Swamp Waters

Despite its location in close proximity to a major metropolitan area (Hampton Roads region of Virginia, population ~1.5 million; Fig. 1), its recognition as the most northern example of a “southern-type” swamp (Mitsch and Gosselink 1993), and its historical and literary significance (e.g., Stowe 1856; Stewart et al. 1979; Royster 1999), remarkably little is known about the hydrology and biogeochemistry of the Great Dismal Swamp. Previous investigations of the Great Dismal Swamp chiefly focused on its ecology, emphasizing phytoplankton in Lake Drummond and select higher organisms (e.g., Garrett and Sonenshine 1979; Marshall 1979; Phillips and Marshall 1993; Lane 2000). Kane (2000), however, recently reported data for some heavy metals (i.e., Pb, Hg, Cr, Ni, Fe) and organic contaminants in surface waters, sediments, and organisms from the swamp. For example, Kane (2000) reported a mean Fe concentration of 44 µmol/kg for seven samples from the White Marsh and Cypress Swamp regions, an Fe concentration of 54 µmol/kg for Washington Ditch water, and a mean Fe concentration of 65 µmol/kg for Lake Drummond waters. Iron speciation, however, was not determined.

The pH of Great Dismal Swamp waters decreases along flow from the upland recharge area west of the Suffolk Scarp, across the Scarp and into the swamp proper (Figs. 1, 2; Table 1). By comparison, DOC concentrations generally increase along flow (Fig. 2). A simple mass balance calculation demonstrates that the waters of Jericho Ditch contribute a significant amount of DOC to waters down-gradient of its confluence with the Washington Ditch (i.e., Jericho-Washington Ditch, Lake Drummond, Feeder Ditch). Using available discharge values for the Washington Ditch (18.4×10^3 m^3/day), Jericho Ditch (61.2×10^3 m^3/day), and the Jericho-Washington Ditch directly down-gradient of their confluence (79.6×10^3 m^3/day; Lichtler and Walker 1979), and our measured DOC concentrations for the Washington and Jericho Ditches (1,030 and 9,600 µmol/kg, respectively), a DOC concentration of 7,619 µmol/kg is estimated for the Jericho-Washington Ditch, which is very similar (a factor of 1.2 larger) to our measured value (i.e., 6,304 µmol/kg; Table 1). The high DOC of Jericho Ditch water is attributed to the thick peat deposits underlying the northwestern region of the swamp (i.e., 3.5 m; Oaks and Whitehead 1979; Lichtler and Walker 1979). A similar mass balance calculation using our pH values for Washington and Jericho Ditches (6.18 and 3.61, respectively; Table 1 and Johannesson et al. 2004) and the discharge estimates of Lichtler and Walker (1979), results in a pH of 4.2 for waters in the Jericho-Washington Ditch, which is identical to our measured value (pH 4.22; Table 1). Consequently, the data suggest that the Jericho Ditch exerts significant controls on both DOC concentrations and pH, and hence, the water quality of Lake Drummond and waters down-gradient of the lake.

Calcium is the dominant cation, on a molal basis, in waters from the upland region west of the Suffolk Scarp, whereas Na exhibits higher concentrations in waters from Lake Drummond and its outflow, the Feeder Ditch (Table 1). Cypress Swamp 2 and Skeeter Crossing, which are the two most up-gradient samples analyzed in our study, are

Ca–Cl–SO_4–HCO_3 waters, whereas other waters from west of the Suffolk Scarp (i.e., Cypress Swamp 1, White Marsh, Washington Ditch) exhibit greater molal HCO_3^- concentrations than SO_4^{2-} (Table 1). Waters from east of the Suffolk Scarp are all Na–Ca–Cl type waters. Molal (Na + K)/Cl ratios of Great Dismal Swamp waters are all close to the seawater ratio ($\sim$0.88) indicating a marine aerosol origin for these ions. By comparison, molal (Ca + Mg)/Cl ratios and SO_4/Cl ratios for Great Dismal Swamp waters range from 5 to 10 and 3 to 14 times higher, respectively, than seawater ratios (i.e., 0.12 and 0.052, respectively), indicating the importance of chemical weathering, adsorption/desorption reactions, and other biogeochemical processes occurring in the drainage basin. The relative decrease in dissolved alkali earth metals (Ca + Mg) compared to alkalis (chiefly Na) along the flow path, for example, likely reflects adsorption of Ca and Mg to organic matter and/or clay minerals in the watershed that does not affect Na to the same degree. That is, Na concentrations remain relatively constant along flow in the Great Dismal Swamp watershed as both Ca and Mg concentrations decrease. Therefore, these relationships do not support simple cation exchange of earth alkalis for alkalis on clay minerals as the dominant process affecting these metals along flow.

Measured alkalinity of waters from east of the Suffolk Scarp, which includes Lake Drummond, range from 64 μmol/kg to 104 μmol/kg (as HCO_3; Table 1). Thermodynamic calculations for Lake Drummond waters (pH 4.3), assuming equilibrium with atmospheric CO_2 ($10^{-3.5}$ atm) and standard conditions (25°C, 1 atm), suggest that carbonate alkalinity (as HCO_3^-) in the lake is on the order of 0.095 μmoles/kg, which is between 600 and 900 times lower than the titration alkalinity. The equilibrium calculations suggest the presence of titratable bases other than carbonate species in these waters. These titratable bases are likely deprotonated acidic functional groups in the dissolved NOM (e.g., see Perdue and Ritchie 2003, and references therein, for a discussion of dissolved NOM contributions to the alkalinity of organic-rich natural waters).

5.2 Arsenic in the Great Dismal Swamp

The strong positive and statistically significant correlation between As(III) and DOC in Great Dismal Swamp waters suggests that DOC may exert important controls on As in these waters (Fig. 4). The distinct relationship between As_T and DOC also reflects the fact that As(III) is the predominant form of As in the organic-rich waters of the swamp. Other investigators have reported relationships between dissolved As and DOC concentrations in natural waters (e.g., Smedley and Kinniburgh 2002; McArthur et al. 2004). The high dissolved As concentrations measured in anaerobic groundwaters from the Huhhot Basin of Inner Mongolia, for example, are associated with high DOC concentrations in addition to high HCO_3, P, NH_4, Fe, and Mn (Smedley et al. 2003). These authors report that As(III) is the dominant form (>60%) of As_T in many of the deep groundwaters from the Huhhot Basin that also have high dissolved organic matter concentrations (DOC up to 30 mg/l; Smedley et al. 2003). Furthermore, they argue that although the relationship between As and DOC, HCO_3, and P concentrations in deep groundwaters of the Huhhot Basin could be coincidental and/or due to their reducing nature and long aquifer residence times, another explanation is that competition between As and organic matter for surface complexation sites on Fe oxide/oxyhydroxides may also be important (Smedley et al. 2003). It should be noted that both the Skeeter Crossing and White Marsh samples exhibit As concentrations that fall outside the 95% confidence interval with regard to their As_T and As(V) relationships with DOC (Fig. 4). The low As concentrations in the Skeeter Crossing sample may reflect adsorptive processes in the local groundwater system, whereas the elevated As(V) in the White Marsh sample may indicate microbial processes in the associated sediments whereby Fe(III) oxides/oxyhydroxides are reduced and previously sorbed As(V) is released to the water column (e.g., Ahmann et al. 1997; Sohrin et al. 1997).

Recent experimental work suggests that dissolved organic matter (i.e., fulvic acid) strongly competes with arsenic anions for surface complexation sites on Fe oxides/oxyhydroxides. Simeoni et al. (2003) investigated the effect of fulvic acid on As(V) adsorption onto both ferrihydrite and gibbsite [i.e., $Al(OH)_3$]. The fulvic acid used in their experiments was extracted from a sand aquifer in New South Wales, Australia. Their experiments showed that surface complexation of As(V) to both ferrihydrite and gibbsite decreased as fulvic acid concentrations increased (Simeoni et al. 2003). Furthermore, they argued that fulvic acid can both displace adsorbed As(V) from ferrihydrite and gibbsite surface sites as well as inhibit adsorption of As(V) to both of these minerals. The ability of fulvic acid to displace adsorbed As(V), and/or inhibit As(V) adsorption, was greatest at pH 4 and decreased with increasing pH (Simeoni et al. 2003). Waters from the Great Dismal Swamp with the highest DOC and As concentrations (i.e., Jericho-Washington Ditch, Lake Drummond, Feeder Ditch) have pH values between 4.2 and 4.3 (Table 1). Consequently, the higher dissolved As concentrations in these Great Dismal Swamp waters may reflect displacement of previously sorbed As from metal oxides/oxyhydroxides and clay mineral surface sites and/or inhibition of As adsorption by the high dissolved organic matter concentrations, both of which are expected to be important in these low pH waters. Unfortunately, the experiments of Simeoni et al. (2003) only involved As(V), and not As(III), which predominates in Great Dismal Swamp waters.

In a series of experiments involving both As(III) and As(V), dissolved NOM collected from a variety of aquatic environments, and the mineral hematite, Redman et al. (2002) showed that dissolved NOM can profoundly affect As mobility in natural waters. Their experiments demonstrate that dissolved NOM can interfere with As adsorption onto hematite. In addition, they report that NOM can potentially oxidize and/or reduce As in the environment. Dissolved NOM also formed aqueous complexes with both As(III) and As(V) in their experiments, with the degree of aqueous complexation increasing as the metal concentration (especially Fe) of the NOM increased (Redman et al. 2002). Their reported relationship with Fe suggests that this metal may act as a bridging cation in As complexation with DOM. Other investigators have reached similar conclusions regarding the probable importance of bridging cations in facilitating As binding with humics (Lin et al. 2004; Warwick et al. 2005; Buschmann et al. 2006). Perhaps the most significant finding of Redman et al. (2002) with regard to As in Great Dismal Swamp waters is that As(III) always exhibited a greater degree of desorption than As(V) from hematite surface sites, and As(III) was more strongly inhibited from adsorbing to hematite than As(V) in the presence of dissolved NOM. These observations are further supported by the recent work of Warwick et al. (2005) and Bauer and Blodau (2006) who also showed that humics inhibit As adsorption to Fe oxides. Consequently, these investigators argued that interaction with dissolved NOM may be partially responsible for the greater tendency of As(III) to be mobilized in the environment compared to As(V) (Redman et al. 2002).

Applying the studies of Redman et al. (2002) and Simeoni et al. (2003) to the Great Dismal Swamp suggests that the high DOC concentrations of surface waters from east of the Suffolk Scarp may, in part, be responsible for their higher As_T concentrations compared to waters from west of the Scarp. In addition, the high DOC concentrations may also explain, to a degree, the predominance of As(III) in these waters. For example, the high DOC concentrations of Great Dismal Swamp waters may promote mobilization of As from

Fe and/or Al oxides/oxyhydroxides, and possibly clay mineral surface sites and more refractory or particulate organic matter, via competitive desorption of previously sorbed As (e.g., Simeoni et al. 2003; Warwick et al. 2005). Again, the work of Redman et al. (2002) indicates that relatively more As(III) desorbs from surface complexation sites compared to As(V). Moreover, once As is in solution, the high DOC concentration of Great Dismal Swamp waters could subsequently act to inhibit As adsorption, especially in the case of As(III) (Redman et al. 2002).

The experiments of Redman et al. (2002) suggest that high DOC concentrations may also promote As(V) reduction in the presence of iron oxides. Although we have not measured iron concentrations or speciation in Great Dismal Swamp waters, the mean dissolved Fe concentration for Lake Drummond waters is reported as 65 μmol/kg (Kane 2000). Thus, the relatively high total Fe concentrations reported for Lake Drummond water may also indicate that microbially mediated reductive dissolution of Fe(III) oxides/oxyhydroxides in lake sediments may be an important process occurring within Lake Drummond. In such a scenario, As adsorbed onto Fe(III) oxides/oxyhydroxides would be released to the water column along with dissolved Fe(II) (e.g., Ahmann et al. 1997). The prevalence of As(III) in the water column may thus reflect either release of previously sorbed As(III) as Fe(III) oxides/oxyhydroxides are reduced by bacteria or direct bacterial reduction of As(V) to As(III) within the lake sediments, followed in either case by release to the water column, both of which could be related to bacterial metabolism of decaying phytoplankton (e.g., Sohrin et al. 1997; Oremland and Stolz 2003, 2005). Future investigations will focus on quantifying the redox conditions of Lake Drummond waters, its sediments, and associated pore waters, including the Fe speciation in the system.

Aqueous complexation of As by NOM may also be significant in Great Dismal Swamp waters (e.g., Thanabalasingam and Pickering 1986). Redman et al. (2002) report both As(III) and As(V) complexation by dissolved NOM in their experiments, and Kalbitz and Wennrich (1998) observed that As mobilization in soil percolation studies was correlated with dissolved organic matter concentrations, suggesting aqueous complexation of As with organic ligands. However, it is not known whether aqueous complexation would stabilize As(III) in solution relative to As(V) in Great Dismal Swamp waters. A recent investigation, for example, suggests that As(V) forms stronger complexes with humic matter than As(III), although at low pH and high DOC concentrations, As(III) was more strongly complexed to humics (Buschmann et al. 2006). Thus, the organic matter-rich, acidic waters of Great Dismal Swamp may represent a natural environment where conditions are right for the preferential formation of strong As(III)–NOM complexes. Although the exact binding mechanism for As complexation to dissolved organic matter remains elusive, as mentioned above, one possibility involves cation bridging between naturally-occurring, dissolved organic ligands and As(III) and/or As(V) (Redman et al. 2002; Lin et al. 2004; Buschmann et al. 2006). Simple ultrafiltration studies may assist in future evaluations of the possible complexation of As with DOM in waters of the Great Dismal Swamp.

Finally, the predominance of As(III) in Great Dismal Swamp waters east of the Suffolk Scarp may reflect intracellular As(V) reduction by phytoplankton followed by excretion of As(III) to the water column (e.g., Andreae 1979, 1983b; Andreae and Klumpp 1979; Sanders 1979; Sanders and Windom 1980; Anderson and Bruland 1991). Both field and laboratory studies have demonstrated that some phytoplankton (e.g., diatoms) can reduce As(V) to As(III) during log phase growth, and further convert inorganic As to methylated species such as MMA and DMA (Sanders and Riedel 1993; Hasegawa et al. 2001; Hellweger et al. 2003). These studies are further supported by others that report the prevalence of As(III) in surface waters during spring, and to lesser extent, autumn phytoplankton blooms (e.g., log phase growth conditions), followed by elevated DMA concentrations in surface waters during the summer (i.e., stationary phase; Howard et al. 1984; Kuhn and Sigg 1993; Aurilio et al. 1994; Sohrin et al. 1997; Hellweger et al. 2003). Owing to the similar chemical properties of the phosphate and arsenate oxyanions, it is generally agreed that phytoplankton and other microbes take up As(V) across their cell membranes via the same phosphate transport system (Oremland Stolz 2003), with As(V) uptake likely reflecting the inability of phytoplankton to discriminate between phosphate and arsenate oxyanions (Hellweger et al. 2003). Furthermore, it is suggested that during spring blooms when phosphorous is not limiting, phytoplankton take up excess PO_4, and hence As(V), in a process referred to as “luxury uptake” (Hellweger et al. 2003). Because the intracellular rate of As(V) reduction is fast compared to rates of arsenic methylation, during luxury uptake, phytoplankton rapidly excrete the accumulating intracellular As(III) to the water column before much of it can be methylated to MMA and/or DMA (Hellweger et al. 2003; Hellweger and Lall 2004). However, during phosphorous-limiting conditions characterized by lower PO_4 and As(V) uptake that typify summer, phytoplankton are able to methylate the lower amounts of intracellular As(III) formed and subsequently excrete MMA and DMA (Hellweger et al. 2003).

Our orthophosphate and As(III) data for Great Dismal Swamp waters are generally consistent with the likelihood that phytoplankton are at least, in part, responsible for some of the As(III) in waters east of the Suffolk Scarp. For example, as water flows into Lake Drummond, PO_4 concentrations along with As(V) concentrations drop, whereas As(III) concentrations rise (Figs. 2, 3; Table 1). These data suggest that phytoplankton in Lake Drummond consume PO_4 along with As(V), reduce As(V) intracellularly, and subsequently excrete As(III) to the lake water. Moreover, diatoms, which are known to reduce As(V) in marine and estuarine waters (e.g., Sanders and Windom 1980), dominate in Lake Drummond waters (the predominant diatom in Lake Drummond is *Asterionella formosa*; Marshall 1979, 2000). Diatoms are followed by cryptomonads (e.g., *Cryptomonas erosa*) in abundance within Lake Drummond, which appear to be more common in summer (Marshall 1979, 2000). Nevertheless, it is important to note that the undetectable levels of MMA and DMA in Lake Drummond waters during the summer (i.e., samples were collected in early July 2001) suggest that other processes (e.g., competition with DOC for adsorptive surface sites, reductive dissolution of Fe oxides with associated As release, complexation with organic ligands) are also likely important in enhancing As(III) concentrations in the swamp waters or that biological processing of As(V) by phytoplankton in Great Dismal Swamp waters is more complex than previous models suggest. Future investigations of the Great Dismal Swamp will examine seasonal variations in As speciation in these waters.

6 Conclusions

Waters of the Great Dismal Swamp are characterized by low pH values and high DOC concentrations. Arsenite, As(III), predominates in surface waters of the Great Dismal Swamp east of the Suffolk Scarp including Lake Drummond, and is strongly correlated to DOC concentrations ($r = 0.94$) and pH ($r = -0.9$). Arsenate, As(V), is more abundant in the inflow waters west of the Suffolk Scarp, and does not exhibit any statistically significant relationships with pH, DOC, or orthophosphate concentrations. Arsenite accounts for 54–81% of the total dissolved As (i.e., As_T) in Lake Drummond and Great Dismal Swamp waters east of the Suffolk Scarp, and between 8% and 37% of As_T in inflow waters west of the scarp. The predominance of As(III) in Great Dismal Swamp waters likely reflects a number of possible processes including competition with DOC for adsorption sites, complexation with dissolved organic ligands, microbially mediated reduction of As(V), and/or uptake of As(V) by phytoplankton followed by intracellular reduction and excretion of As(III) to the water column. Further investigations are planned to better characterize the biogeochemistry of As in waters of the Great Dismal Swamp.

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