THE ROLE OF HEADWATER WETLANDS IN ALTERING STREAMFLOW AND CHEMISTRY IN A MAINE, USA CATCHMENT[1]

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ABSTRACT: Headwater wetlands, including hillside seeps, may contribute to downstream systems disproportionately to their relatively small size. We quantified the hydrology and chemistry of headwater wetlands in a central Maine, USA, catchment from 2003 to 2005 to determine their role in maintaining headwater streamflow and in affecting stream chemistry. A few of these headwater wetlands, commonly referred to as "seeps," were characterized by relatively high groundwater discharge. During summer base flow, seeps were the primary source of surface water to the stream, contributing between 40 and 80% of stream water. Comparisons of groundwater and surface water dominant ion chemistry revealed only slight differences at the bedrock interface; however, significant changes occurred at the shallow groundwater-surface water interface where we found decreases in total and individual cation concentrations with decreasing depth. Seep outflows significantly increased total cation and calcium concentrations in streams. Outflows at two seeps produced relatively high nitrate concentrations (88 ± 15 and 93 ± 15 μg/l respectively), yet did not correspond to higher nitrate in stream water below seep outflows (2 ± 1 μg/l). We demonstrate that small wetlands ($< 1{,}335$ m^2) can contribute to headwater stream processes by linking groundwater and surface-water systems, increasing the duration and magnitude of stream discharge, and by affecting stream chemistry, particularly during periods of base flow.

(KEY TERMS: seeps; groundwater slope wetlands; wetland functions; nitrate; first-order streams.)

INTRODUCTION

Headwater wetlands extend aquatic habitat farther into higher topographic positions within the landscape and can influence the temporal and spatial movement and chemistry of water by changing groundwater residence time within catchments (Hill and Devito, 1997; Brown *et al.*, 1999). Although they occupy a small portion of a catchment (typically < 10%), these wetlands can substantially contribute to surface-water flow for example, by increasing stream hydroperiod (Healy and Pack, 1983; Ashby *et al.*, 1998). This has a profound effect on how these systems function in the landscape, especially because headwater wetlands may contribute up to 50% of the groundwater entering secondary streams from the riparian zone (Warwick and Hill, 1988; Sklash, 1990) and increase total surface-water flow during the summer low-flow period (Uchida *et al.*, 2003). Because changes in flow paths and variations in source areas regulate stream chemistry (Peterson *et al.*, 2001;

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Lowe and Likens, 2005), these wetlands influence downstream processes by moderating low-flow conditions and contributing to stream-water chemistry.

There have been numerous studies examining shallow groundwater interactions with surface water (SGW-SW) in glaciated regions of North America. These studies have identified important influencing factors such as catchment geology and geomorphology (Devito et al., 1996; Stein et al., 2004), soil conditions that alter water movement (Harr, 1977), groundwater residence time within subsurface layers (Hill and Devito, 1997; Winter, 2007), and catchment land use (Whigham and Jordan, 2003). Commonly, SGW-SW interaction studies are associated with near-stream riparian environments (Hill, 2000; Angier and McCarty, 2008). Headwater wetlands, and in particular groundwater slope wetlands (which include "seeps"), have received less attention, especially those indirectly connected to surface-water bodies.

Headwater uplands act as critical groundwater recharge areas. Water traveling through these areas interacts with the vegetation, soils, and geologic materials, and influences the chemistry of streams (Meyer and Wallace, 2001; Sidle et al., 2001; Lowe and Likens, 2005). Wetlands in headwater areas can serve as a conduit for the transfer of subsurface water to headwater streams. In areas with shallow till over bedrock with low permeability, as found in the northern United States and in our study area, most groundwater flow comprised local flow regimes (Toth, 1962; Roulet, 1990; Hill and Devito, 1997). Within catchments, small areas of high groundwater discharge, such as seeps, can exert a strong influence on streamflow and patterns of element retention within wetlands in relation to associated streams (Hill and Devito, 1997; Angier and McCarty, 2008). We investigated the role of headwater wetlands in a region likely dominated by local flow regimes to assess the hydrological and chemical contributions of wetlands to headwater streams. If hydrologic contributions are as significant as those reported in other systems (Warwick and Hill, 1988; Sklash, 1990; Alexander et al., 2007), these wetlands are integral to the functioning of headwater areas. Therefore, it may be prudent to examine existing headwater management policies to ensure protection of these traditionally under-protected systems (Nadeau and Rains, 2007).

From 2003 to 2005, we examined the hydrology and water chemistry of three headwater wetlands in a central Maine, USA, catchment to quantify the dominant ion chemistry among three common headwater wetland types, to ascertain the relative importance of seeps in maintaining low streamflow conditions, and to determine their role in stream-water flow and chemistry in a headwater system dominated by local flow regimes.

STUDY SITE

The study area is located in the Uplands portion of the New England physiographic province in northwestern Hancock County, Maine, USA (44°54′ N, 68°21′ W) approximately 8 km north of Amherst, Maine (Figure 1). The entire catchment is approximately 300 ha and discharges into the West Branch of the Union River north of Maine Route 9. It is bounded to the north by Springy Brook Mountain and to the south by Dutton Pond. The catchment is underlain by the Lucerne Granite, one of the larger granitic plutons in New England (672 km^2), and is composed of quartz plagioclase, alkali-feldspar, and biotite (Wones and Ayuso, 1993).

Soils within the catchment are classified within the Dixfield-Marlow-Brayton general soil association and characterized by very deep, nearly level to steep,
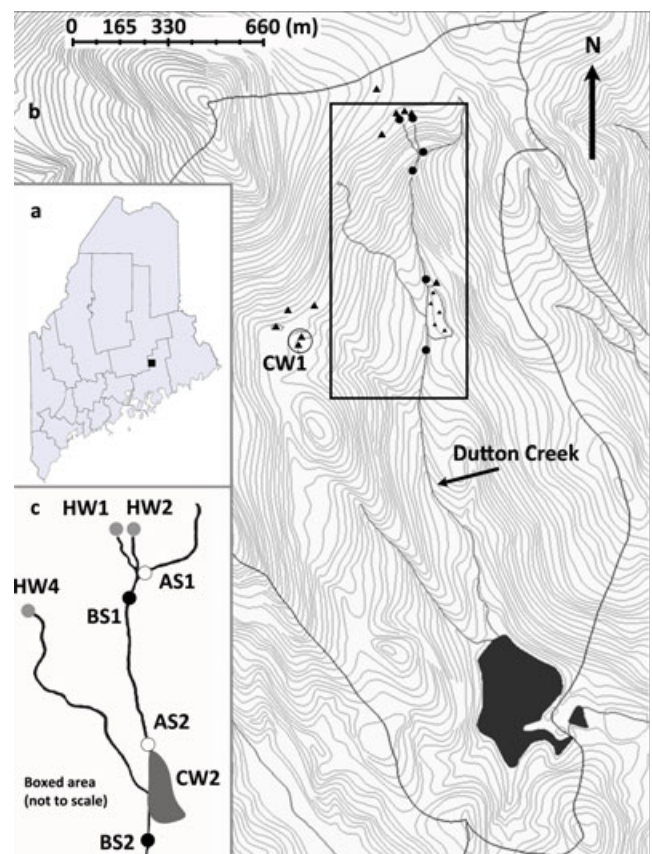

FIGURE 1. Site and Sampling Locations Within a Central Maine, USA Catchment. Regional location within Maine (a, black dot); research catchment, wetlands, and sampling locations (b, contour interval 3 m); and surface-water sampling overview (c, not to scale). Stream surface-water sampling sites are white and black dots, while wetlands and wetland surface-water sampling sites are in gray. AS, above seep; BS, below seep; triangles, piezometer locations; circles, surface-water collection points.

well-drained to poorly drained, sandy to gravelly fine sandy loam formed from compact till (USDA, 1998). Although a formal soil survey has not been completed for this area, local soils are likely classified as Marlow fine sandy loam. These soils occur on side slopes of till ridges and are normally associated with Dixfield soils at the toe-slopes. A perched high water table is common on these soils during the spring (USDA, 1998). Overstory vegetation in the catchment is generally composed of northern deciduous American beech (*Fagus grandiflora*, Ehrh.) and sugar maple (*Acer saccharum,* Marsh.) hardwoods, and scattered stands of red spruce (*Picea rubens*, Sarg.) and balsam fir (*Abies balsamea*, L.) (Morley and Calhoun, 2009). The completely forested catchment was harvested over 40 years ago.

The catchment contains three distinct headwater wetland types: groundwater slope wetlands (HW1, HW2, HW4; herein referred to as "seeps") characterized by permanent groundwater discharge along sloping (~12°) terrain, a "bench wetland" (CW1) located at a break in slope resulting in a small flat area within a larger hillslope, and a "toe-slope" wetland (CW2) exhibiting seepage at the base of a slope (Figure 1b).

METHODS

Groundwater

At three wetlands (HW1, CW1, and CW2), we manually installed six piezometer clusters (consisting of two piezometers per cluster) using a split-spoon core sampler or bucket auger. Piezometer clusters had one piezometer installed to bedrock or at 4 m (herein referred to as top of bedrock or "ToB"), while the second was placed approximately 0.6 m below ground surface (shallow groundwater, herein referred to as "SGW"). We positioned one piezometer cluster in the seep, and remaining piezometers at distances sufficient to determine horizontal hydraulic and chemical gradients, ranging from 10 to 100 m. Piezometers were constructed with 2.54 cm outside diameter (OD) PVC pipe with 30.48 cm long machine-slotted screens (0.0254 cm) placed at the base of the piezometer. We placed a sand pack around the screen and bentonite pellets above the sand pack to isolate it, and the remainder of the opening was backfilled with excavated soil mixed with bentonite to prevent movement of water along the annulus of the piezometer.

We measured hydraulic head in the piezometers bimonthly, May through November, from 2003 through 2005 and calculated vertical and horizontal hydraulic gradients to establish groundwater flow directions during biologically active time periods. Piezometer positions were determined with two Ashtech duel frequency GPS units (Ashtech, Santa Clara, CA, USA) with submeter accuracy. The hydraulic conductivity of the geologic materials was determined by displacing a volume of water in the piezometers and measuring the rate of recovery using the formula from Hvorslev (1951),

$$K = \frac{r_c^2 \ \ln(R_e/R_s)}{2lT_0}, \tag{1}$$

where K is the hydraulic conductivity, r_c is the radius of the piezometer, R_s is the radius of the piezometer screen, R_e is the effective radius (assumed to be $200*R_s$) (Butler, 1998), l is the screen length, and T_0 is the lag time, the time it takes the piezometer to recover 37% of the initial head. We calculated discharge rates using Darcy's Law (Fetter, 2000). Three Telog WLS-31 data loggers (Telog Instruments, Victor, NY, USA) with 5-psi pressure transducers were placed to monitor water levels. We placed one in the ToB piezometer at the head of seep HW1. Two others were placed at the base of v-notched weirs at HW1 and HW4.

To evaluate groundwater flow, it was important to ascertain hydrological inputs into the catchment. Precipitation data were taken from the Bear Brook Watershed in Maine (BBWM) long-term monitoring station, 21 km east of the study site, and local National Oceanic and Atmospheric Administration (NOAA) precipitation records for Orono, Maine (NOAA, 2007). The BBWM monitoring station utilizes an Aerochem metrics wet/dry precipitation collector (Aerochem Metrics, Inc., Bushnell, FL, USA).

Surface Water

At two seeps (HW1 and HW4), we diverted surface flow into 90° v-notched weirs and measured discharge bimonthly by measuring stage and recording the time it took to fill a 150-ml beaker. This was repeated several times to generate a mean, with seep discharge determined from rating curves developed with the discharge and water-elevation data. The position of a third toe-slope seep (CW2), lengthwise along the eastern bank of Dutton Creek prevented direct discharge measurements. At each of four locations along Dutton Creek (AS1, BS1, AS2, and BS2), we concurrently measured stream stage and stream velocity during base-flow periods using a tape measure and current meter suspended at 60% of the maximum stream depth (Carter and Davidian, 1968). The discharge was calculated from the stream area and water

velocity. During low-flow conditions, we constrained surface-water flows through a 10.2 cm-diameter PVC pipe to measure discharge. All discharge measurements were then compared to stream stage to develop an empirical relationship between stage and discharge. We used this seasonal flow data to determine the amount of discharge to the headwater stream system. These monitoring periods coincided with groundwater measurements. Finally, watershed areas for HW1, HW2, AS1, and BS1 were calculated by digitally tracing the watershed perimeters, with the areas of these polygons used with seasonal base-flow discharges to estimate runoff.

Water Chemistry

All water samples were laboratory-filtered with 0.45-μm cellulose filters (Fisherbrand, Pittsburg, PA, USA, cat. no. 09-719-2E) and analyzed at the University of Maine's Environmental Chemistry Laboratory (ECL) for acid anions (NO_3^-, SO_4^{2-}, Cl^-) and reactive phosphorus (as orthophosphate) using ion chromatography, base cations (Ca^{2+}, K^+, Na^+, Mg^{2+}) and trace elements (Al^{3+}, Be^{2+}, Fe^{2+}, Mn^{2+}, Si^+) via ICP-AES, and inorganic nitrogen (NO_2/NO_3^-, NH_4^+) and total nitrogen (TDN) using an ALPKEM auto-analyzer (Perstorp Analytical Company, Wilsonville, OR, USA) within 24 h of sampling. We collected all water samples in plastic high-density polyethylene bottles except samples for orthophosphate, which were collected in amber glass bottles. Sample containers were cleaned in a 10% HCl bath for at least 24 h, rinsed three times with distilled water, and rinsed once with Milli-Q high resistivity water. The bottles were air dried, and then capped until use. We measured pH (Hanna Instruments HI 9025; Hanna Instruments Inc., Woonsocket, RI, USA), dissolved oxygen (YSI model 55; YSI Inc., Yellow Springs, OH, USA), water

temperature, and specific conductance (YSI model 30) bimonthly, coincident with groundwater and surface-water monitoring periods.

For groundwater collection, we purged all piezometers of water by removing at least three case volumes, or bailed dry when recovery was slow. We collected water samples the following day with a 2.2-cm outside diameter (OD) clear PVC sample bailer (Atlantic Screen and Manufacturing Inc., Milton, DE, USA). We stored all samples in a cooler with ice packs, and rinsed the bailer between samples with deionized water to remove sample water.

Surface-water collection sites were located at seep outflows (HW1, HW2, and HW4) and at Dutton Creek (AS1, AB1, AS2, and BS2) (Figure 1). Seep surface-water samples were collected near the point where the diffuse seepage began to form a first-order stream and upstream from the weir to minimize aeration of water. Surface-water samples were taken in Dutton Creek at two locations above and below seep outflow. We placed the sample container directly in the creek and allowed water to flow into the sample container to minimize sediments entering the sample bottle. We collected surface-water and groundwater samples three times during the growing season (after spring leaf-out, mid-summer, and before dormancy).

Data Analysis

To determine the relationship between seep outflows and surface waters, water chemistry data were analyzed using analysis of variance (ANOVA). Contrasts of total and individual ion chemistry among wetlands and by sample depth (ToB, SGW, and surface water, Table 1) were analyzed using ANOVA with an alpha level of 0.05, unless the sample size was < 30. In these situations, the alpha level was set

TABLE 1. Summary of Groundwater and Surface-Water Samples Taken in a Maine Headwater Catchment From May 2003 to November 2005.

Sample	Wetland Type (ID)	Piezometer Type	Total Locations	Sampled Locations	Sample *n*
Groundwater	Seeps (HW1, HW2, HW4)	ToB	3	2	8
		SGW	4	4	26
	Bench (CW1)	ToB	3	3	5
		SGW	3	3	12
	Toe-slope (CW2)	ToB	5	5	15
		SGW	5	5	32
	Uplands	ToB	6	4	7
		SGW	6	3	4
Surface Water	Seep outflows		3	3	27
	Stream		4	4	28
	Total				164

Notes: ToB, top of bedrock (piezometer installed to bedrock interface); SGW, shallow groundwater (installed at 0.6 m below ground surface).

at 0.01 (Quinn and Keough, 2002). For ANOVA tests, we used Tukey's *post hoc* test to determine group similarities. Normality of each variable (ion) was assessed using box-plots and Kolmogorov-Smirnov tests, with all data log transformed to meet assumptions of normality (Quinn and Keough, 2002). Samples from one date were not analyzed for ANC and these data were not included in the anion statistical analysis, thus resulting in uneven sample sizes. A *post hoc* Bonferroni test checked for equity of variances among groupings. Samples with ion concentrations below analytical detection limits were assigned a value of half of the detection limit for analysis (Hedin *et al.*, 1998). Those data not meeting the above normality tests (discharge contrasts) were analyzed using a Wilcoxon signed-rank test. We used SYSTAT (v.12; SYSTAT, Inc.) for all statistical analysis.

RESULTS

Precipitation

Annual precipitation into the catchment was 1,240, 850, and 1,520 mm from 2003 to 2005, respectively, throughout the study period (Navrátil *et al.*, 2010). The higher annual precipitation in 2003 and 2005 was characterized by exceptionally high early spring (March) and late-year (October) rainfall. Long-term precipitation trends in Maine average 97 mm per month, or 1,160 mm yearly, and are generally characterized by even amounts of precipitation throughout the year (NOAA, 2007). In 2005, a mean of 127 mm of precipitation per month occurred at BBWM research area and confirmed by data obtained from a NOAA weather station 24 km west of the study site in Orono, Maine.

Groundwater

Seep groundwater (via piezometric surface elevation change) responded quickly to precipitation events (Figure 2). Furthermore, the hydrograph indicates distinct seasonal and diurnal response of groundwater to precipitation inputs due to evapotranspiration. Water levels were higher during fall and spring dormant periods, while throughout the growing season, groundwater upwelling sustained saturated conditions in seeps, with the discharged groundwater typically forming first-order streams. At the head of the seep, an upward hydraulic gradient existed throughout a majority of the monitoring period with
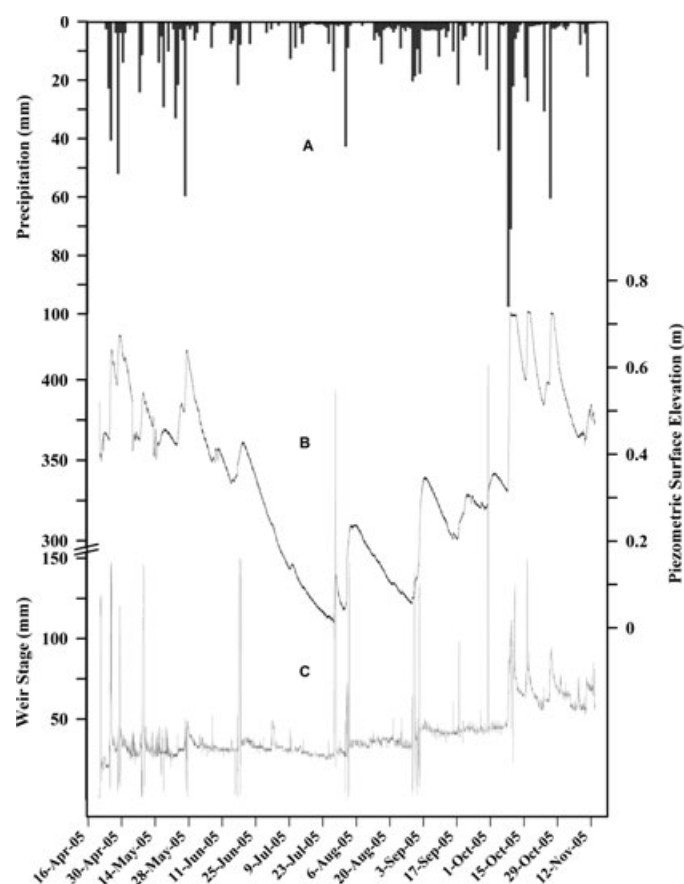

FIGURE 2. Seep HW1 Groundwater Hydrograph and Weir Stage Response to Precipitation Events in 2005. Precipitation (A) is daily totals, groundwater (B) and weir stage (C) data were recorded at 10-min intervals. Precipitation data taken from the Bear Brook Watershed Maine research catchment, 21 km east of the study site.

both ToB and SGW piezometers exhibiting artesian conditions (Figure 3). Approximately 10 m downstream from the seeps, SGW had higher hydraulic head than deeper groundwater indicating groundwater recharge.

The majority of the six piezometer clusters placed in the adjacent uplands detected groundwater only during occasional spring and late-year monitoring. Only two upland piezometers, those near the seeps, recorded groundwater for sufficient periods to calculate adequately upland groundwater discharge. Hydraulic conductivity measured in shallow piezometers installed in seeps ranged from 9.3×10^{-4} to 1.3×10^{-6} m/s. Hydraulic conductivity of ToB piezometers in seeps ranged from 2.3×10^{-6} to 9.0×10^{-7} m/s.

Surface Water

Similarly to groundwater responses, discharge at weir outflows responded quickly to storm events
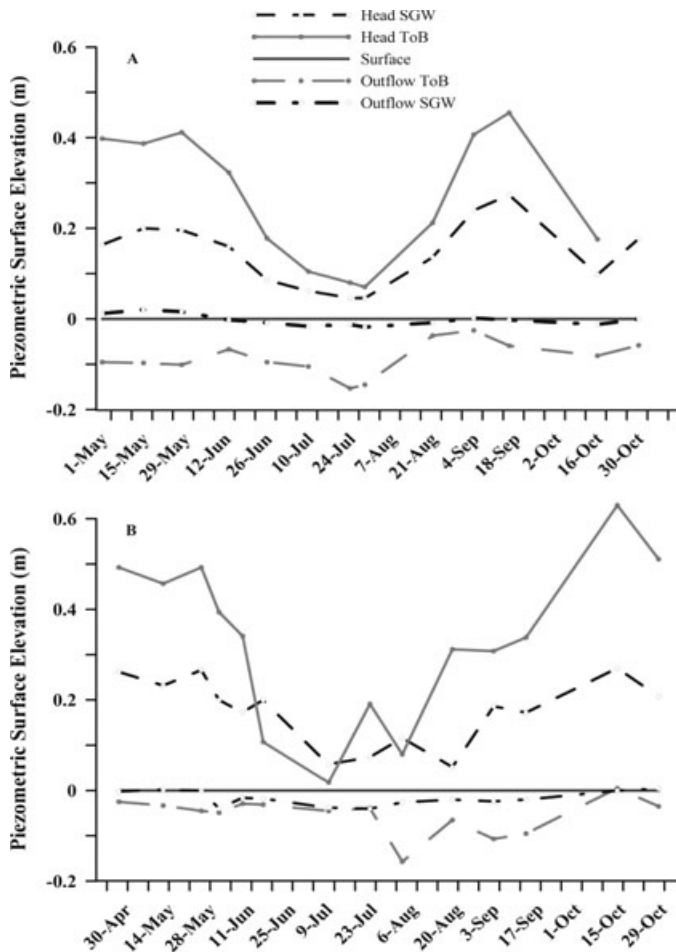
FIGURE 3. Groundwater Head at Seepage Head and Outflow of Seep HW1. Data show top of bedrock (ToB) (0.7-2.5 m) and shallow (0.6 m) piezometers at the seep head and seep outflow in 2004 (A) and 2005 (B).
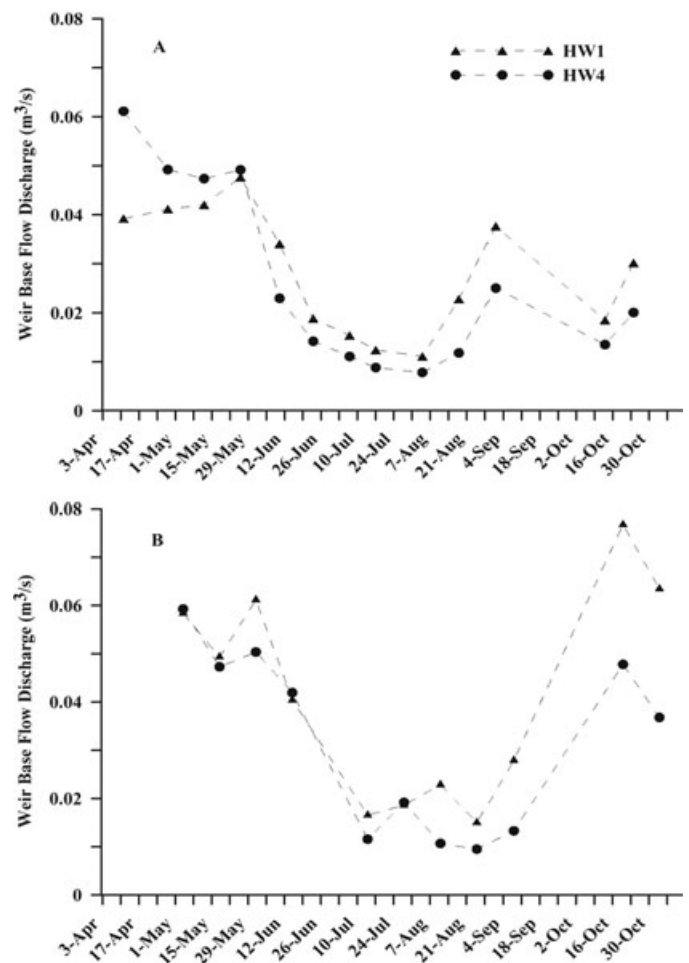

FIGURE 4. Seasonal Trend of Surface-Water Discharge From Wetlands HW1 and HW4. Data measured at 90° v-notched weirs during base flow in 2004 (A) and 2005 (B).

(Figure 2). Surface-water base-flow discharge at seep outflows also varied seasonally (Figure 4). Higher discharges occurred in spring and fall during dormant periods of vegetation growth and followed trends in groundwater hydraulic head. A correlation of groundwater hydraulic head with seep weir discharge from HW1 indicated a high association ($r^2 = 0.926$) between the two parameters. In 2005, discharge ranged from a high of 0.077 m^3/s (46.1 l/min), following a large precipitation event in the fall, to 0.009 m^3/s (5.7 l/min) during summer low-flow periods.

Discharge measurements at four locations along Dutton Creek allowed for two upstream-downstream (Above Seep [AS], Below Seep [BS]) comparisons in relation to seep outflows. During low-flow periods, discharge measurements could not be made above the seepage outflow due to a lack of surface water. At the first location (AS1, BS1) (Figure 1), mean stream discharge above the seep was 0.037 m^3/s

ranging from < 0.001 to 0.118 m^3/s. Below seep outflow, mean stream discharge was 0.082 m^3/s and ranged from 0.014 to 0.146 m^3/s (Figure 5). Stream discharge below seep outflow was always higher than above seep outflows using both direct instream discharge measurements and runoff calculations. Stream discharge measurements indicated that seeps contributed 49% of stream base flow on average and ranged from 11 to 89% of total base flow in the stream with highest relative contribution during periods of low flow (Figure 5). Area-weighted runoff discharge calculations (stream discharge/drainage area) indicated that seeps had greater discharge per area than either the area above the seep (AS1) or the associated uplands above the BS1 monitoring point (Wilcoxon rank-sum, $Z = -2.934$, $p < 0.001$) (Table 2).

Seep discharge at a second location approximately 550 m downstream (AS2, BS2) (Figure 1) did not
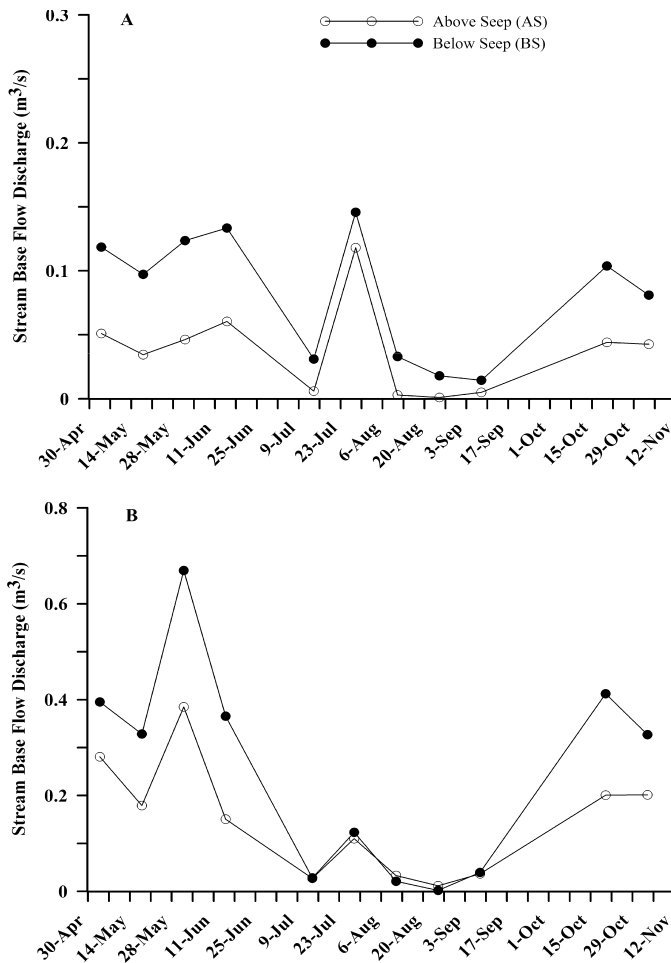
FIGURE 5. Stream Discharge Above and Below Seep Outflow. Discharge above (open circles) and below (closed circles) seep outflows at two locations: upper AS1-BS1 (A) and lower AS2-BS2 (B) outflows during base flow.

Groundwater Chemistry

Overall trends in total ions across a gradient of piezometer depth indicate a decrease in ion concentration from ToB to surface water (SW); however, this difference was only significant at the SGW-SW comparison (Table 3). Total cations decreased with decreasing depth (ANOVA, $F = 2$, 22.9, $p < 0.05$). Comparison of each groundwater sample depth to surface water (ToB $\times$ SW and SGW $\times$ SW) were all significantly lower ($p < 0.01$), whereas the comparison between groundwater depths (ToB $\times$ SGW) was not ($p = 0.056$). Furthermore, the decrease in ion concentration with decreasing depth was not as strong for total anions. A significant difference by depth was found, however, only for the SGW $\times$ SW interaction ($F = 2$, 4.3, $p < 0.05$). There was no effect of depth between ToB $\times$ SW ($p = 0.347$) and ToB $\times$ SGW ($p = 1.00$).

We detected differences among the three wetland types (and the associated upland) for total cations, but no differences for total anions. Specifically, total cation concentration in ToB piezometers was significantly different across wetland types (ANOVA, $F = 3$, 4.7, $p < 0.05$); however, comparisons indicated that only the CW1 $\times$ Upland (UPL) comparison was significant ($p < 0.05$). All other comparisons of the ToB samples indicated no difference in total cations at this depth. Total cation concentration was significantly different among wetland types in SGW piezometers ($F = 3$, 18.5, $p < 0.05$). At this depth, all interactions were significant except for CW1 $\times$ UPL and Seep $\times$ UPL ($p = 1.00$, 0.308 respectively). For total anions, groundwater samples at ToB and SGW depths were not significantly different across wetland types ($F = 3$, 0.2, $p = 0.917$; $F = 3$, 2.6, $p = 0.059$ respectively).

Seep and Surface-Water Chemistry

Calcium and sodium were the dominant cations in seep outflow and in stream waters (Table 3). Calcium concentrations at seeps (mean $\pm$ SE; 143.8 $\pm$ 5.6 µeq/l) represented 50% of total cations in water. Sodium concentration at seeps (99.2 $\pm$ 3.7 µeq/l) represented 35% of total cations in water. Two seeps (HW1 and HW2) separated by approximately 10 m show significant

increase streamflow to the extent of the upper seeps. Mean stream discharge above the seep was 0.15 m³/s and ranged from 0.01 to 0.39 m³/s. Below the seep, mean stream discharge was 0.25 m³/s and ranged from < 0.01 to 0.67 m³/s, representing a 25% increase (overall) in streamflow from the seepage area. During high flow periods, discharge below the seepage area always increased. However, during low-flow periods discharge decreased below the seep relative to stream discharge above the seep of up to 35%.

TABLE 2. Runoff and Discharge Summary of Upland and Wetland Area Above Sampling Site BS1.

Site*	Drainage Area (m²)	Total Area (%)	Mean Discharge (m³/s)	Mean Runoff (mm/h)	Range (mm/h)
AS1	72,787	52	3.7×10^{-2}	1.85	0.14-3.56
BS1	55,472	39	8.0×10^{-2}	5.19	1.85-8.52
HW1 and HW2	12,627	9	4.1×10^{-2}	26.48	12.26-40.69

*Refer to Figure 1.

TABLE 3. Summary of Ion Chemistry in a Maine, USA Headwater Catchment.

Water Type	Area		HCO_3^- mg/l	Ca^{2+} mg/l	Cl^- mg/l	K^+ mg/l	Mg^{2+} mg/l	Na^+ mg/l	NH_4^+ mg/l	NO_3^- µg/l of N	PO_4^{3-} µg/l as P	SO_4^{2-} mg/l as S	TD N mg/l of N
ToB	Upland	n	6	7	7	7	7	7	7	7	7	7	7
		Mean (SD)	11.1 (6.6)	2.3 (1.2)	3.1 (1.6)	0.6 (0.4)	0.5 (0.2)	4.1 (3.3)	0.2 (0.3)	27.0 (52.7)	7.1 (9.3)	1.3 (0.3)	0.4 (0.6)
	Seep	n	6	8	8	8	8	8	8	8	8	8	8
		Mean (SD)	18.4 (22.4)	6.7 (3.5)	2.6 (1.0)	0.8 (0.2)	1.4 (0.8)	4.9 (3.1)	0.1 (0.1)	25.3 (33.3)	3.9 (1.7)	0.8 (0.6)	0.4 (0.2)
	Toe	n	7	15	15	15	15	15	15	15	15	15	15
		Mean (SD)	20.1 (8.1)	5.9 (2.8)	5.0 (9.3)	3.8 (12.3)	1.4 (0.6)	4.6 (1.1)	0.1 (0.2)	13.1 (8.6)	12.6 (11.5)	1.4 (2.0)	0.5 (0.3)
	Bench	n	5	5	5	5	5	5	5	5	5	5	5
		Mean (SD)	12.0 (18.9)	2.2 (0.9)	2.3 (0.3)	0.5 (0.3)	0.5 (0.2)	5.3 (93.7)	0.2 (0.3)	2.1 (1.7)	2.3 (0.9)	1.1 (0.5)	0.4 (0.3)
SGW	Upland	n	3	4	4	4	4	4	4	4	4	4	4
		Mean (SD)	5.6 (1.0)	1.6 (0.4)	1.7 (0.3)	0.4 (0.1)	0.3 (0.1)	3.1 (2.0)	<0.1 (<0.1)	8.9 (4.7)	2.9 (2.6)	1.3 (0.1)	0.3 (0.3)
	Seep	n	19	26	26	26	26	26	25	26	25	26	25
		Mean (SD)	11.8 (8.0)	4.2 (3.6)	2.4 (1.2)	0.7 (0.5)	0.6 (0.6)	5.0 (7.5)	0.1 (0.1)	19.3 (21.6)	5.5 (5.5)	0.9 (0.5)	0.3 (0.2)
	Toe	n	15	32	32	32	32	32	32	32	32	32	32
		Mean (SD)	16.2 (9.5)	4.6 (2.2)	2.8 (2.7)	1.5 (4.2)	0.9 (0.4)	6.2 (5.2)	0.7 (90.5)	6.8 (5.4)	7.8 (3.8)	0.5 (0.8)	1.0 (0.4)
	Bench	n	12	12	12	12	12	12	12	12	12	12	12
		Mean (SD)	4.3 (3.9)	1.2 (0.4)	2.5 (2.2)	1.0 (2.6)	0.2 (0.1)	2.1 (0.5)	<0.1 (<0.1)	2.0 (1.7)	2.2 (2.3)	1.5 (0.5)	0.2 (0.1)
Surface	Stream	n	25	28	28	28	28	28	28	28	28	28	25
		Mean (SD)	5.5 (3.6)	2.3 (0.9)	1.6 (0.1)	0.2 (0.1)	0.5 (0.1)	2.3 (0.5)	<0.1 (<0.1)	19.7 (30.0)	2.0 (0.9)	1.1 (0.2)	0.2 (0.1)
	Seep	n	24	27	27	27	27	27	27	27	27	27	26
		Mean (SD)	6.9 (3.2)	2.9 (0.6)	1.5 (0.1)	0.3 (0.1)	0.4 (0.1)	2.3 (0.4)	<0.1 (<0.1)	64.4 (52.2)	4.1 (5.8)	1.3 (0.1)	0.2 (0.1)

Notes: Data organized by water depth and wetland/upland location for all piezometers in the catchment. ToB, top of bedrock (0.7-2.5 m below ground surface); SGW, shallow groundwater (0.6 m below ground surface); Seep, includes sites HW1, HW2, HW4; Toe, includes site CW2; Bench, includes site CW1.

TABLE 4. Surface-Water Chemistry (mean ± SE) of Selected Ions at Two Seep Outflows (HW1, HW2),
and Above (AS1) and Below (BS1) Confluence With a First-Order Stream.

Cations	n	pH	Na^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	K^+ mg/l	NH_4^+ mg/l	Total Cations μeq/l
HW1	9	5.49 ± 0.11	2.22 ± 0.2	2.61 ± 0.2[a]	0.37 ± 0.02[a]	0.28 ± 0.02	ND	264.83 ± 19.0
HW2	9	5.88 ± 0.14	2.56 ± 0.1	3.28 ± 0.1[b]	0.52 ± 0.01[b]	0.30 ± 0.02	ND	324.83 ± 9.3
AS1	5	5.67 ± 0.05	1.99 ± 0.2	1.22 ± 0.1[A]	0.36 ± 0.04	0.12 ± 0.02	ND	179.80 ± 14.0
BS1	7	5.83 ± 0.04	2.18 ± 0.2	2.01 ± 0.3[B]	0.43 ± 0.04	0.15 ± 0.01	ND	324.33 ± 23.3

Anions	n	HCO_3^- mg/l	Cl^- mg/l	SO_4^{2-} mg/l	NO_3^- μg/l	PO_4^{3-} μg/l	ANC μeq/l	Total Anions μeq/l
HW1	9	5.87 ± 1.1[a]	1.49 ± 0.03	1.35 ± 0.01	88.29 ± 15.2	5.49 ± 3.2	115.13 ± 14.7[a]	235.22 ± 23.7
HW2	9	8.68 ± 1.3[b]	1.43 ± 0.03	1.36 ± 0.02	93.17 ± 14.9	4.92 ± 1.0	170.29 ± 2.9[b]	299.70 ± 11.2
AS1	5	3.38 ± 1.0	1.62 ± 0.04	1.27 ± 0.03	1.00 ± 0.0	1.56 ± 0.3	58.02 ± 16.8	172.42 ± 17.4
BS1	7	3.96 ± 1.1	1.56 ± 0.05	1.27 ± 0.02	2.01 ± 0.7	1.54 ± 0.3	81.56 ± 16.2	226.31 ± 25.5

Notes: ND, nondetected. Lower case superscripts indicate significant difference between seeps; uppercase indicate significant difference above and below seep outflow. Wilcoxon test ($p < 0.05$).

differences in cation and anion contribution (Table 3). Most importantly, seep outflows at HW1 and HW2 produced relatively high nitrate concentrations (88.3 ± 15.2 and 93.2 ± 14.9 μg/l respectively), representing approximately 30% of the total anion charge balance in seep waters. This is in contrast to stream-water anion charge contributions (approximately 1%) both above and below seeps.

Seep Contribution to Surface Waters

Seeps significantly increased total ion concentration below seepage outflow (Wilcoxon, $Z = 3.342$, $p < 0.05$, Table 4). Total cation concentration below seepage outflow was significantly higher (mean 54.5 μeq/l; $Z = 2.023$, $p < 0.05$) (Table 2). Mean calcium concentrations increased (39.5 ± 10.7 μeq/l) downstream from the seep and this increase was significant ($Z = 2.023$, $p < 0.05$). However, sodium was not significantly increased downstream ($Z = 0.674$, $p = 0.5$). Mean total anion concentration in seeps (235 and 300 μeq/l) was higher than mean stream waters above seep outflow (172 μeq/l), though stream-water anion concentration below seep outflow was not significantly different from its above-seep counterpart ($Z = 1.21$, $p = 0.225$). In addition, the relatively high nitrate in seepage outflows did not correspond to significantly higher nitrate in stream water below seep outflow (2.0 ± 0.7 μeq/l).

DISCUSSION

Residence time of groundwater within a catchment depends on catchment geology, topography, climate, and soil depth and type in similarly sized catchments (Burns et al., 1998; Burns and Kendall, 2002; McGuire and McDonnell, 2006; Soulsby et al., 2007). The rapid response of the seeps in this study to precipitation events is indicative of rapid channeling of subsurface waters from adjacent upland areas and can result from a mixing of low residence time of SGW with event water. In this study, discharge at several groundwater slope wetlands (HW1, HW4, and HW2) is sustained by shallow, subsurface water forced to the surface by a shallower soil depth and a low permeability layer (bedrock) preventing downward flow. Hydraulic conductivities for the shallow piezometers (at 60 cm depth) (10^{-4}-10^{-5} m/s) and deeper ToB piezometers (10^{-6}-10^{-7} m/s) are similar to conductivities reported in other headwater wetland complexes. For example, Devito et al. (1996) reported hydraulic conductivities of 10^{-5}-10^{-6} m/s at 20-30 cm depths and 10^{-6}-10^{-7} m/s at depths of 200 cm. The head of these seeps did not exhibit variable saturated contributing or "source" areas (Dunne and Black, 1970), as we observed no increase in the aerial extent of the seeps, only an increase in the level of inundation and discharge. This indicates a reduced effect from overland flow and further emphasizes the presence of strong preferential subsurface flow paths. The piezometer cluster comparison between the seep head and seep outflow (Figure 3), and the strong association between groundwater hydraulic head and seep discharge indicates that the wetland is a groundwater discharge wetland (Brinson, 1993). Furthermore, given its location in the landscape, this wetland supplies water for groundwater recharge downgradient from the wetland and therefore can influence discharge-recharge relationships in headwater areas (Sophocleous, 2002).

Hydrologic contribution from seep outflow to the stream (as a percentage of total flow) was substantial,

especially during periods of base flow in the upper seep (AS1-BS1) comparison. Stream discharge below the outflow was always higher than above seep outflows indicating the importance of seeps contributing to streamflow during periods of base flow. Because we did not make seep-stream contrasts during or immediately following rain events, we cannot speculate on the relative inputs these wetlands have on streamflow during storm events, when the majority of water flows through stream systems. Furthermore, the hydrologic contribution of these seeps is only realized at higher geomorphic positions within the catchment because relative contributions are not as substantial to larger stream waters as evidenced by the discharge comparison made farther downstream. The measured losses during low-flow conditions at the downstream (AS2-BS2) location could be a result of a reduced capacity to affect larger flow systems, or a result of several near-stream mechanisms which include losses to deeper groundwater, a change in conductivity of streambed substrate (e.g., large cobbles), or rerouting of a portion of the channel. Either of these conditions could reduce the amount of surface water at the stream where we took discharge measurements. However, this study is consistent with other reports that estimate from 30 to over 70% of stream-water inputs can originate from groundwater discharge wetlands (Warwick and Hill, 1988; Sklash, 1990; Cole et al., 1997; Uchida et al., 2003; Soulsby et al., 2006; Alexander et al., 2007). Therefore, these wetlands can substantially augment headwater streamflow since first-order streams can contribute over 70% of the mean water volume of second-order streams (Alexander et al., 2007). During a year of high rainfall, runoff calculations highlighted the disproportionate contribution to flow from these wetlands contributing up to 80% of stream water during low-flow periods. The landscape above both AS1 and the two seeps appears similar, with no obvious distinctions in the slope, geology, or forest structure, also known to influence hillslope dynamics (Roulet, 1990; Hill and Devito, 1997; Sidle et al., 2001; Sophocleous, 2002; Stein et al., 2004; Soulsby et al., 2006, 2007).

This study contrasted groundwater chemistry of three different wetland types (and the associated upland) within a small headwater catchment and found few differences among groundwater samples at the bedrock interface. Most of the chemical changes that did occur were among comparisons of SGW within 0.6 m of the ground surface and highlights the influence of these areas on chemical processing, much like hyphoreic zones in stream channels (Naiman et al., 2005). Of the three wetland types studied here, the groundwater slope or seepage wetlands influenced surface-water chemistry by large contributions of ions from within this biologically active layer.

Higher calcium concentrations from the ToB piezometers indicate a source of calcium from groundwater likely via weathering of bedrock. Organic soils have high cation exchange capacity, with calcium readily exchanged over other base cations on exchange sites and thus can be mobilized during precipitation events which could explain a short-term and likely much smaller source of calcium from these seeps (Mitsch and Gosselink, 2000). However, the majority probably comes from calcium-rich groundwater traveling along the bedrock interface (Hill, 1993; Pierson and Taylor, 1994). Further, relatively high concentrations of beryllium in seep outflows (up to 3 µg/l, data not shown) also provide evidence of extended bedrock contact (Morley, 2008).

This study found significant differences in base cation concentrations among wetland types and at the SGW-SW interface, yet these results were not paired with like changes in acid anion concentration. We would expect acid anions to reflect similar changes in water chemistry as base cations. This discrepancy could result from the presence of anionic dissolved organic carbon (DOC). We did not specifically measure DOC in this study, therefore, we are unable to directly infer the role of DOC in our system. However, charge balance for all water samples were within 2.5% of equivalence (except for a single sample date where ANC was not analyzed) which suggests that the contribution of DOC in this system is likely low. However, this small difference could in effect cause some of our anion samples to be nonsignificant because our anion contrast between ToB and SGW samples were nearly significant ($p = 0.059$). Generally, groundwater DOC concentrations at headwater seepage outflows and similar small streams are quite low (Kaplan and Newbold, 2000; Inamdar et al., 2004), even in water traveling through shallow subsurface (or phreatic) pathways (McDowell and Likens, 1988) although, see Cronan and Aiken (1985). The emergence of this water in the seep, which contains organic soils, could add a source of DOC. However, we believe that any contribution would be low given the rate of discharge from this seep, the close charge balance of the sample water, and the relative clarity of the water at the point of discharge.

High nitrate concentrations have been found in other studies of groundwater discharge wetlands in the northeast (Burns, 1998; West et al., 2001; Burns and Kendall, 2002). McHale et al. (2002) found that high stream-water nitrate concentrations coincided with peaks in the groundwater contribution discharging from till at high topographic positions in the landscape. However, nitrate concentrations were low in ToB groundwater, likely a result of denitrification due to reduced conditions, or to uptake by vegetation. Burns (1998) suggests that high nitrate

levels of springs are a result of older groundwater from deep flow paths entering below the rooting zone, particularly in areas of bedrock fractures. The extent to which fractures affect groundwater flow paths in this research area is not known. The area upslope of the seeps contain thin soils over granite bedrock. The effect of deep groundwater on nitrate concentrations is likely low given the placement of these sites near the top of the catchment, 185 m away and only 7 m higher. Furthermore, the ToB nitrate concentrations were not statistically different from the SGW samples, as only the SGW-SW comparison was significant. This indicates contributions from within the seep itself, or as a result of a mixture of groundwater interacting with well aerated soils from within the seep. High nitrate concentrations emanating from biologically active soils have been reported elsewhere, supporting the likelihood of a similar effect at the study site (Bowden, 1987; Cirmo and McDonnell, 1997). In addition, ^{15}N values for these groundwater and surface-water samples did not indicate highly enriched (denitrifying) conditions in ToB or SGW samples as $\delta^{15}NO_3$-N concentrations at these locations were only slightly enriched (+10.6 ± 2.6 and +6.3 ± 0.9‰, respectively), whereas seep outflows indicated isotopic mixing of these waters (+8.5 ± 1.5‰) (Terry R. Morley, unpublished data, 2005). Corresponding stream-water values at Dutton Creek (<+2‰) are lower than concentrations found in similar northeastern streams, which average approximately +5‰ (Mayer et al., 2002). We therefore feel that these groundwater slope wetlands, during the growing season, provide a constant source of cooler groundwater, readily available for mineralization and nitrification by the large organic soil layer at these seepage wetland sites. We did not observe an increase in stream-water nitrate concentration such as those found in groundwater discharge areas in near-stream environments (i.e., Angier and McCarty, 2008) as we believe the longitudinal length from seep outflow to the stream (over 100 m) at the study site probably consumes the relatively high nitrate levels at seep outflows such that it does not affect stream-water chemistry (Simon et al., 2010).

flows to headwater streams during periods of low flow. The effects of this in our study are two-fold. First, it extends aquatic habitat for wetland-dependent biota farther into headwater reaches, and secondly it maintains water flow during a period when water levels and temperatures could threaten survival of aquatic organisms. This has important consequences for headwater stream biota including sustenance of freshwater fisheries (Labbe and Fausch, 2000), stream invertebrates (Orendt, 2000; Collins et al., 2007), vegetation communities (Hall et al., 2001), and amphibian populations (Gomi et al., 2002; Morley, 2008). We found that groundwater flow paths in headwaters can be concentrated into relatively small areas, such as in seeps, which if located high in the catchment can contribute up to 80% of runoff during base-flow periods. Due to the emergence of this subsurface water, seeps also provide a source of base cations and alkalinity to surface waters thereby buffering downstream systems from acidic conditions common during precipitation events. These base cations can help maintain cation exchange saturation and allow resorption of exchangeable base cations onto exchange sites farther downstream. This is important for streams with low acid neutralizing capacity, as is common in headwaters regions. The concentrated groundwater discharge at the head of these wetlands results in increased surface-water discharge and ion contributions to the first-order stream. However, the results of this study are conservative because our seeps were located approximately 100 m from the stream. Seeps located closer to surface-water bodies would increase streamflow and ion contribution more than those in this study.

The cumulative effect of headwater wetlands in similar hydrologic landscapes may be substantial considering estimates of headwater streams in the United States and Europe range from 50 to over 75% of total stream length (Leopold et al., 1964; Krecek and Haigh, 2006; Nadeau and Rains, 2007). Seeps in headwaters regions function to increase the length of the aquatic environment in the landscape, and increase the duration of surface-water supply to these streams while buffering stream-water chemistry.

CONCLUSIONS

This study demonstrates that water-forming headwater seepage areas in our study area in eastern Maine are influenced by SGW, and provides important hydrological functions to headwater regions. The primary function is the sustenance of surface-water

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