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The role of headwater wetlands in altering stream flow and chemistry in a Maine, USA catchment

Terry R. Morley¹, A. S. Reeve², Aram J.K. Calhoun³

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 - 2005 to determine their role in maintaining headwater stream flow 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 $\mu\text{g/l}$ respectively), yet did not correspond to higher nitrate in stream water below seep outflows (2 ± 1 $\mu\text{g/l}$). 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.)

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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 less than 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; 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

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2
3 wetlands, and in particular groundwater slope wetlands (which include ‘seeps’), have received
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5 less attention, especially those indirectly connected to surface-water bodies.
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9 Headwater uplands act as critical groundwater recharge areas. Water traveling through
10
11 these areas interacts with the vegetation, soils, and geologic materials, and influences the
12
13 chemistry of streams (Meyer and Wallace, 2001; Sidle *et al.*, 2001; Lowe and Likens, 2005).
14
15 Wetlands in headwater areas can serve as a conduit for the transfer of subsurface water to
16
17 headwater streams. In areas with shallow till over bedrock with low permeability, as found in the
18
19 northern United States and in our study area, most groundwater flow is comprised of local flow
20
21 regimes (Toth, 1962; Roulet, 1990; Hill and Devito, 1997). Within catchments, small areas of
22
23 high groundwater discharge, such as seeps, can exert a strong influence on stream flow and
24
25 patterns of element retention within wetlands in relation to associated streams (Hill and Devito,
26
27 1997; Angier and McCarty, 2008). We investigated the role of headwater wetlands in a region
28
29 likely dominated by local flow regimes to assess the hydrological and chemical contributions of
30
31 wetlands to headwater streams. If hydrologic contributions are as significant as those reported in
32
33 other systems (Warwick and Hill, 1988; Sklash, 1990; Alexander *et al.*, 2007), these wetlands
34
35 are integral to the functioning of headwater areas. Therefore, it may be prudent to examine
36
37 existing headwater management policies to ensure protection of these traditionally under-
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39 protected systems (Nadeau and Rains, 2007).
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47 From 2003 - 2005, we examined the hydrology and water chemistry of three headwater
48
49 wetlands in a central Maine, USA, catchment to quantify the dominant ion chemistry among
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51 three common headwater wetland types, to ascertain the relative importance of seeps in
52
53 maintaining low stream-flow conditions, and to determine their role in stream-water flow and
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55 chemistry in a headwater system dominated by local flow regimes.
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STUDY SITE

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6 The study area is located in the Uplands portion of the New England physiographic
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8 province in northwestern Hancock County, Maine, USA (44° 54' N 68° 21' W) approximately 8
9
10 km north of Amherst, Maine (Figure 1). The entire catchment is approximately 300 ha and
11
12 discharges into the West Branch of the Union River north of Maine Route 9. It is bounded to the
13
14 north by Springy Brook Mountain and to the south by Dutton Pond. The catchment is underlain
15
16 by the Lucerne Granite, one of the larger granitic plutons in New England (672 km²), and is
17
18 composed of quartz plagioclase, alkali-feldspar, and biotite (Wones and Ayuso, 1993).
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23 Soils within the catchment are classified within the Dixfield-Marlow-Brayton general soil
24
25 association and characterized by very deep, nearly level to steep, well-drained to poorly-drained,
26
27 sandy to gravelly fine sandy loam formed from compact till (USDA, 1998). Although a formal
28
29 soil survey has not been completed for this area, local soils are likely classified as Marlow fine
30
31 sandy loam. These soils occur on side slopes of till ridges and are normally associated with
32
33 Dixfield soils at the toe-slopes. A perched high water table is common on these soils during the
34
35 spring (USDA, 1998). Overstory vegetation in the catchment is generally composed of northern
36
37 deciduous American beech (*Fagus grandiflora*, Ehrh.) and sugar maple (*Acer saccharum*,
38
39 Marsh.) hardwoods, and scattered stands of red spruce (*Picea rubens*, Sarg.) and balsam fir
40
41 (*Abies balsamea*, L.) (Morley and Calhoun, 2009). The completely forested catchment was
42
43 harvested over 40 years ago.
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49 The catchment contains three distinct headwater wetland types: groundwater slope
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51 wetlands (HW1, HW2, HW4; herein referred to as 'seeps') characterized by permanent
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53 groundwater discharge along sloping (~ 12°) terrain, a 'bench wetland' (CW1) located at a break
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3 in slope resulting in a small flat area within a larger hillslope, and a ‘toe-slope’ wetland (CW2)
4
5 exhibiting seepage at the base of a slope (Figure 1b).
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7

8 9 METHODS

10 11 12 Groundwater

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14
15 At three wetlands (HW1, CW1, CW2), we manually installed six piezometer clusters
16
17 (consisting of two piezometers per cluster) using a split-spoon core sampler or bucket auger.
18
19 Piezometer clusters had one piezometer installed ‘to bedrock’ or at four meters (herein referred
20
21 to as top of bedrock or ‘ToB’), while the second was placed approximately 0.6 m below ground
22
23 surface (shallow groundwater, herein referred to as ‘SGW’). We positioned one piezometer
24
25 cluster in the seep, and remaining piezometers at distances sufficient to determine horizontal
26
27 hydraulic and chemical gradients, ranging from 10 to 100 m. Piezometers were constructed with
28
29 2.54 cm outside diameter (OD) PVC pipe with 30.48 cm long machine-slotted screens (0.0254
30
31 cm) placed at the base of the piezometer. We placed a sand pack around the screen and bentonite
32
33 pellets above the sand pack to isolate it, and the remainder of the opening was backfilled with
34
35 excavated soil mixed with bentonite to prevent movement of water along the annulus of the
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37 piezometer.
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44 We measured hydraulic head in the piezometers bimonthly, May through November,
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46 from 2003 through 2005 and calculated vertical and horizontal hydraulic gradients to establish
47
48 groundwater flow directions during biologically active time periods. Piezometer positions were
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50 determined with two Ashtech dual frequency GPS units with sub-meter accuracy. The hydraulic
51
52 conductivity of the geologic materials was determined by displacing a volume of water in the
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3 piezometers and measuring the rate of recovery using the formula from Hvorslev (1951),
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$$K = \frac{r_c^2 \ln(Re/Rs)}{2lT_0} \quad [1]$$

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11 where K is the hydraulic conductivity, r_c is the radius of the piezometer, R_s is the radius of the
12 piezometer screen, R_e is the effective radius (assumed to be $200 * R_s$) (Butler, 1998), l is the
13 screen length, and T_0 is the lag time, the time it takes the piezometer to recover 37% of the initial
14 head. We calculated discharge rates using Darcy's Law (Fetter, 2000). Three Telog WLS-31 data
15 loggers with 5 psi pressure transducers were placed to monitor water levels. We placed one in
16 the ToB piezometer at the head of seep HW1. Two others were placed at the base of v-notched
17 weirs at HW1 and HW4.
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29 In order to evaluate groundwater flow, it was important to ascertain hydrological inputs
30 into the catchment. Precipitation data were taken from the Bear Brook Watershed in Maine
31 (BBWM) long-term monitoring station, 21 km east of the study site, and local NOAA
32 precipitation records for Orono, Maine (NOAA, 2007). The BBWM monitoring station utilizes
33 an Aerochem metrics wet/dry precipitation collector.
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40 41 42 Surface Water

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44 At two seeps (HW1, HW4), we diverted surface flow into 90° v-notched weirs and measured
45 discharge bi-monthly by measuring stage and recording the time it took to fill a 150 ml beaker.
46
47 This was repeated several times to generate a mean, with seep discharge determined from rating
48 curves developed with the discharge and water-elevation data. The position of a third toe-slope
49 seep (CW2), lengthwise along the eastern bank of Dutton Creek prevented direct discharge
50 measurements. At each of four locations along Dutton Creek (AS1, BS1, AS2, BS2), we
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3 concurrently measured stream stage and stream velocity during base flow periods using a tape
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5 measure and current meter suspended at 60% of the maximum stream depth (Carter and
6
7 Davidian, 1968). The discharge was calculated from the stream area and water velocity. During
8
9 low flow conditions, we constrained surface water flows through a 10.2 cm diameter PVC pipe
10
11 to measure discharge. All discharge measurements were then compared to stream stage to
12
13 develop an empirical relationship between stage and discharge. We used this seasonal flow data
14
15 to determine the amount of discharge to the headwater stream system. These monitoring periods
16
17 coincided with groundwater measurements. Finally, watershed areas for HW1, HW2, AS1, and
18
19 BS1 were calculated by digitally tracing the watershed perimeters, with the areas of these
20
21 polygons used with seasonal base-flow discharges to estimate runoff.
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27 28 Water Chemistry

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30 All water samples were laboratory-filtered with 0.45 μm cellulose filters (Fisherbrand 09-
31
32 719-2E) and analyzed at the University of Maine's Environmental Chemistry Laboratory (ECL)
33
34 for acid anions (NO_3^- , SO_4^{2-} , Cl^-) and reactive phosphorus (as orthophosphate) using ion
35
36 chromatography, base cations (Ca^{2+} , K^+ , Na^+ , Mg^{2+}) and trace elements (Al^{3+} , Be^{2+} , Fe^{2+} , Mn^{2+} ,
37
38 Si^+) via ICP-AES, and inorganic nitrogen ($\text{NO}_2^-/\text{NO}_3^-$, NH_4^+) and total nitrogen (TDN) using an
39
40 ALPKEM auto-analyzer within 24h of sampling. We collected all water samples in plastic High
41
42 Density Polyethylene (HDPE) bottles except samples for orthophosphate, which were collected
43
44 in amber glass bottles. Sample containers were cleaned in a 10% HCl bath for at least 24 h,
45
46 rinsed three times with distilled water, and rinsed once with Milli-Q high resistivity water. The
47
48 bottles were air dried, and then capped until use. We measured pH (Hanna Instruments HI 9025),
49
50 dissolved oxygen (YSI model 55), water temperature, and specific conductance (YSI model 30)
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52 bimonthly, coincident with groundwater and surface-water monitoring periods.
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3 For groundwater collection, we purged all piezometers of water by removing at least
4 three case volumes, or bailed dry when recovery was slow. We collected water samples the
5 following day with a 2.2 cm outside diameter (OD) clear PVC sample bailer (Atlantic Screen and
6 Manufacturing Inc.). We stored all samples in a cooler with ice packs, and rinsed the bailer
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13 between samples with deionized water to remove sample water.
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15
16 Surface-water collection sites were located at seep outflows (HW1, HW2, HW4) and at
17 Dutton Creek (AS1, AB1, AS2, BS2) (Figure 1). Seep surface-water samples were collected near
18 the point where the diffuse seepage began to form a first order stream and upstream from the
19 weir to minimize aeration of water. Surface-water samples were taken in Dutton Creek at two
20 locations above and below seep outflow. We placed the sample container directly in the creek
21 and allowed water to flow into the sample container to minimize sediments entering the sample
22 bottle. We collected surface-water and groundwater samples three times during the growing
23 season (after spring leaf-out, mid-summer and before dormancy).
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34 Data analysis

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36 To determine the relationship between seep outflows and surface waters, water chemistry data
37 were analyzed using analysis of variance (ANOVA). Contrasts of total and individual ion
38 chemistry among wetlands and by sample depth (ToB, SGW, and surface water) were analyzed
39 using ANOVA with an alpha level of 0.05, unless the sample size was less than 30. In these
40 situations, the alpha level was set at 0.01 (Quinn and Keough, 2002). For ANOVA tests, we used
41 Tukey's post-hoc test to determine group similarities. Normality of each variable (ion) was
42 assessed using box-plots and Kolmogorov-Smirnov tests, with all data log transformed to meet
43 assumptions of normality (Quinn and Keough, 2002). Samples from one date were not analyzed
44 for ANC and these data were not included in the anion statistical analysis, thus resulting in
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3 uneven sample sizes. A *post-hoc* Bonferroni test checked for equity of variances among
4
5 groupings. Samples with ion concentrations below analytical detection limits were assigned a
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7 value of half of the detection limit for analysis (Hedin *et al.*, 1998). Those data not meeting the
8
9 above normality tests (discharge contrasts) were analyzed using a Wilcoxon signed-rank test. We
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11 used SYSTAT (v.12, SYSTAT, Inc.) for all statistical analysis.
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13
14

15 16 RESULTS

17 18 19 Precipitation

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21 Annual precipitation into the catchment was 1240 mm, 850 mm, and 1520 mm from 2003 to
22
23 2005, respectively, throughout of the study period (Navrátil *et al.*, 2010). The higher annual
24
25 precipitation in 2003 and 2005 were characterized by exceptionally high early spring (March)
26
27 and late year (October) rainfall. Long-term precipitation trends in Maine average 97 mm per
28
29 month, or 1160 mm yearly, and are generally characterized by even amounts of precipitation
30
31 throughout the year (NOAA, 2007). In 2005, a mean of 127 mm of precipitation per month
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33 occurred at Bear Brook Watershed Maine (BBWM) research area and confirmed by data
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35 obtained from a NOAA weather station 24 km west of the study site in Orono, Maine.
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40 41 Groundwater

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43 Seep groundwater (via piezometric surface elevation change) responded quickly to
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45 precipitation events (Figure 2). Furthermore, the hydrograph indicates distinct seasonal and
46
47 diurnal response of groundwater to precipitation inputs due to evapotranspiration. Water levels
48
49 were higher during fall and spring dormant periods, while throughout the growing season,
50
51 groundwater upwelling sustained saturated conditions in seeps, with the discharged groundwater
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53 typically forming first order streams. At the head of the seep, an upward hydraulic gradient
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existed throughout a majority of the monitoring period with both ToB and SGW piezometers exhibiting artesian conditions at the head of the seep (Figure 3). Approximately ten meters downstream from the seeps, shallow groundwater 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 adequately calculate 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 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 $0.077 \text{ m}^3/\text{s}$ (46.1 l/min), following a large precipitation event in the fall, to $0.009 \text{ m}^3/\text{s}$ (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

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2
3 above the seep was $0.037 \text{ m}^3/\text{s}$ ranging from < 0.001 to $0.118 \text{ m}^3/\text{s}$. Below seep outflow, mean
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5 stream discharge was $0.082 \text{ m}^3/\text{s}$ and ranged from 0.014 to $0.146 \text{ m}^3/\text{s}$ (Figure 5). Stream
6
7 discharge below seep outflow was always higher than above seep outflows using both direct in-
8
9 stream discharge measurements and runoff calculations. Stream discharge measurements
10
11 indicated that seeps contributed 49% of stream base flow on average and ranged from 11 to 89%
12
13 of total base flow in the stream with highest relative contribution during periods of low-flow
14
15 (Figure 5). Area-weighted runoff discharge calculations (stream discharge / drainage area)
16
17 indicated that seeps had greater discharge per area than either the area above the seep (AS1) or
18
19 the associated uplands above the BS1 monitoring point (Wilcoxon rank-sum, $Z = -2.934$, $P <$
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21 0.001) (Table 2).
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28 Seep discharge at a second location approximately 550 m downstream (AS2, BS2)
29
30 (Figure 1) did not increase stream flow to the extent of the upper seeps. Mean stream discharge
31
32 above the seep was $0.15 \text{ m}^3/\text{sec}$ and ranged from 0.01 to $0.39 \text{ m}^3/\text{sec}$. Below the seep, mean
33
34 stream discharge was $0.25 \text{ m}^3/\text{sec}$ and ranged from < 0.01 to $0.67 \text{ m}^3/\text{sec}$, representing a 25%
35
36 increase (overall) in stream flow from the seepage area. During high flow periods, discharge
37
38 below the seepage area always increased. However, during low flow periods discharge decreased
39
40 below the seep relative to stream discharge above the seep of up to 35%.
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45 Groundwater Chemistry

46
47 Overall trends in total ions across a gradient of piezometer depth indicate a decrease in
48
49 ion concentration from ToB to surface water (SW); however, this difference was only significant
50
51 at the SGW – SW comparison (Table 3). Total cations decreased with decreasing depth
52
53 (ANOVA, $F = 2, 22.9$, $P < 0.05$). Comparison of each groundwater sample depth to surface
54
55 water (ToB x SW and SGW x SW) were all significantly lower ($P < 0.01$), whereas the
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3 comparison between groundwater depths (ToB x SGW) was not ($P = 0.056$). Furthermore, the
4
5 decrease in ion concentration with decreasing depth was not as strong for total anions. A
6
7 significant difference by depth was found, however only for the SGW x SW interaction ($F = 2$,
8
9 4.3 , $P < 0.05$). There was no effect of depth between ToB x SW ($P = 0.347$) and ToB x SGW (P
10
11 $= 1.00$).

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14
15 We detected differences among the three wetland types (and the associated upland) for
16
17 total cations, but no differences for total anions. Specifically, total cation concentration in ToB
18
19 piezometers was significantly different across wetland types (ANOVA, $F = 3$, 4.7 , $P < 0.05$),
20
21 however comparisons indicated that only the CW1 x Upland (UPL) comparison was significant
22
23 ($P < 0.05$). All other comparisons of the ToB samples indicated no difference in total cations at
24
25 this depth. Total cation concentration was significantly different among wetland types in SGW
26
27 piezometers ($F = 3$, 18.5 , $P < 0.05$). At this depth, all interactions were significant except for
28
29 CW1 x UPL and Seep x UPL ($P = 1.00$, 0.308 respectively). For total anions, groundwater
30
31 samples at ToB and SGW depths were not significantly different across wetland types ($F = 3$,
32
33 0.2 , $P = 0.917$; $F = 3$, 2.6 , $P = 0.059$ respectively).

34 35 36 37 38 39 40 Seep and Surface Water Chemistry

41
42 Calcium and sodium were the dominant cations in seep outflow and in stream waters
43
44 (Table 3). Calcium concentrations at seeps, (mean \pm SE; 143.8 ± 5.6 $\mu\text{eq/l}$) represented 50% of
45
46 total cations in water. Sodium concentration at seeps (99.2 ± 3.7 $\mu\text{eq/l}$) represented 35% of total
47
48 cations in water. Two seeps (HW1, HW2) separated by approximately ten meters show
49
50 significant differences in cation and anion contribution (Table 3). Most importantly, seep
51
52 outflows at HW1 and HW2 produced relatively high nitrate concentrations (88.3 ± 15.2 and 93.2
53
54 ± 14.9 $\mu\text{g/l}$ respectively), representing approximately 30% of the total anion charge balance in
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3 seep waters. This is in contrast to stream-water anion charge contributions (approximately one
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5 percent) both above and below seeps.
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9 Seep contribution to surface waters

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11 Seeps significantly increased total ion concentration below seepage outflow (Wilcoxon, Z
12 = 3.342, $P < 0.05$). Total cation concentration below seepage outflow was significantly higher
13
14 (mean 54.5 $\mu\text{eq/l}$; $Z = 2.023$, $P < 0.05$) (Table 2). Mean calcium concentrations increased ($39.5 \pm$
15
16 $10.7 \mu\text{eq/l}$) downstream from the seep and this increase was significant ($Z = 2.023$, $P < 0.05$).
17
18 However, sodium was not significantly increased downstream ($Z = 0.674$, $P = 0.5$). Mean total
19
20 anion concentration in seeps (235 $\mu\text{eq/l}$ and 300 $\mu\text{eq/l}$) were higher than mean stream waters
21
22 above seep outflow (172 $\mu\text{eq/l}$), though stream-water anion concentration below seep outflow
23
24 was not significantly different from its above-seep counterpart ($Z = 1.21$, $P = 0.225$). In addition,
25
26 the relatively high nitrate in seepage outflows did not correspond to significantly higher nitrate in
27
28 stream water below seep outflow ($2.0 \pm 0.7 \mu\text{eq/l}$).
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36 DISCUSSION

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38
39 Residence time of groundwater within a catchment depends on catchment geology,
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41 topography, climate, and soil depth and type in similarly sized catchments (Burns and Kendall,
42
43 2002; Burns *et al.*, 1998; McGuire and McDonnell, 2006; Soulsby *et al.*, 2007). The rapid
44
45 response of the seeps in this study to precipitation events is indicative of rapid channeling of
46
47 subsurface waters from adjacent upland areas and can result from a mixing of low residence time
48
49 of shallow groundwater with event water. In this study, discharge at several groundwater slope
50
51 wetlands (HW1, HW4 and HW2) is sustained by shallow, subsurface water forced to the surface
52
53 by a shallower soil depth and a low permeability layer (bedrock) preventing downward flow.
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3 Hydraulic conductivities for the shallow piezometers (at 60 cm depth) (10^{-4} to 10^{-5} m/s) and
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5 deeper ToB piezometers (10^{-6} to 10^{-7} m/s) are similar to conductivities reported in other
6
7 headwater wetland complexes. For example, Devito *et al.* (1996) reported hydraulic
8
9 conductivities of 10^{-5} to 10^{-6} m/s at 20-30 cm depths and 10^{-6} to 10^{-7} m/s at depths of 200 cm. The
10
11 head of these seeps did not exhibit variable saturated contributing or 'source' areas (Dunne and
12
13 Black, 1970), as we observed no increase in the aerial extent of the seeps, only an increase in the
14
15 level of inundation and discharge. This indicates a reduced effect from overland flow and further
16
17 emphasizes the presence of strong preferential subsurface flow paths. The piezometer cluster
18
19 comparison between the seep head and seep outflow (Figure 3), and the strong association
20
21 between groundwater hydraulic head and seep discharge indicates that the wetland is a
22
23 groundwater discharge wetland (Brinson, 1993). Furthermore, given its location in the landscape,
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25 this wetland supplies water for groundwater recharge downgradient from the wetland and
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27 therefore can influence discharge – recharge relationships in headwater areas (Sophocleous,
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29 2002).
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37 Hydrologic contribution from seep outflow to the stream (as a percentage of total flow)
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39 was substantial, especially during periods of base flow in the upper seep (AS1-BS1) comparison.
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41 Stream discharge below the outflow was always higher than above seep outflows indicating the
42
43 importance of seeps contributing to stream flow during periods of base flow. Because we did not
44
45 make seep - stream contrasts during or immediately following rain events, we cannot speculate
46
47 on the relative inputs these wetlands have on stream flow during storm events, when the majority
48
49 of water flows through stream systems. Furthermore, the hydrologic contribution of these seeps
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51 is only realized at higher geomorphic positions within the catchment because relative
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53 contributions are not as substantial to larger stream-waters as evidenced by the discharge
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3 comparison made farther downstream. The measured losses during low-flow conditions at the
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5 downstream (AS2-BS2) location could be a result of a reduced capacity to affect larger flow
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7 systems, or a result of several near-stream mechanisms which include losses to deeper
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9 groundwater, a change in conductivity of streambed substrate (e.g., large cobbles), or rerouting
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11 of a portion of the channel. Either of these conditions could reduce the amount of surface water
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13 at the stream where we took discharge measurements. However, this study is consistent with
14
15 other reports that estimate between 30 to over 70% of stream water inputs can originate from
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17 groundwater discharge wetlands (Warwick and Hill, 1988; Sklash, 1990; Cole *et al.*, 1997;
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19 Uchida *et al.*, 2003; Soulsby *et al.*, 2006; Alexander *et al.*, 2007). Therefore, these wetlands can
20
21 substantially augment headwater stream flow since first-order streams can contribute over 70%
22
23 of the mean water volume of second-order streams (Alexander *et al.*, 2007). During a year of
24
25 high rainfall, runoff calculations highlighted the disproportionate contribution to flow from these
26
27 wetlands contributing up to 80% of stream water during low-flow periods. The landscape above
28
29 both AS1 and the two seeps appears similar, with no obvious distinctions in the slope, geology,
30
31 or forest structure, also known to influence hillslope dynamics (Roulet, 1990; Hill and Devito,
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33 1997; Sidle *et al.*, 2001; Sophocleous, 2002; Stein *et al.*, 2004; Soulsby *et al.*, 2006; 2007).

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41 This study contrasted groundwater chemistry of three different wetland types (and the
42
43 associated upland) within a small headwater catchment and found few differences among
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45 groundwater samples at the bedrock interface. Most of the chemical changes that did occur were
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47 among comparisons of SGW within 0.6 m of the ground surface and highlights the influence of
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49 these areas on chemical processing, much like hyporeic zones in stream channels (Naiman *et*
50
51 *al.*, 2005). Of the three wetland types studied here, the groundwater slope or seepage wetlands
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3 influenced surface water chemistry by large contributions of ions from within this biologically
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5 active layer.
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9 Higher calcium concentrations from the ToB piezometers indicate a source of calcium
10 from groundwater likely via weathering of bedrock. Organic soils have high cation exchange
11 capacity, with calcium readily exchanged over other base cations on exchange sites and thus can
12 be mobilized during precipitation events which could explain a short-term and likely much
13 smaller source of calcium from these seeps (Mitsch and Gosselink, 2000). However, the majority
14 likely comes from calcium rich groundwater travelling along the bedrock interface (Hill, 1993;
15 Pierson and Taylor, 1994). Further, relatively high concentrations of beryllium in seep outflows
16 (up to 3 µg/l, data not shown) also provide evidence of extended bedrock contact (Morley,
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18 2008).
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30 This study found significant differences in base cation concentrations among wetland
31 types and at the SGW-SW interface, yet these results were not paired with like changes in acid
32 anion concentration. We would expect acid anions to reflect similar changes in water chemistry
33 as base cations. This discrepancy could result from the presence of anionic dissolved organic
34 carbon (DOC). We did not specifically measure DOC in this study therefore, we are unable to
35 directly infer the role of DOC in our system. However, charge balance for all water samples were
36 within 2.5% of equivalence (except for a single sample date where ANC was not analyzed)
37 which suggests that the contribution of DOC in this system is likely low. However, this small
38 difference could in effect cause some of our anion samples to be non significant because our
39 anion contrast between ToB and SGW samples were nearly significant ($P = 0.059$). Generally,
40 groundwater DOC concentrations at headwater seepage outflows and similar small streams are
41 quite low (Kaplan and Newbold, 2000; Inamdar *et al.*, 2004), even in water travelling through
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3 shallow subsurface (or phreatic) pathways (McDowell and Likens, 1988) although, see Cronan
4 and Aiken (1985). The emergence of this water in the seep, which contains organic soils, could
5
6 add a source of DOC. However, we believe that any contribution would be low given the rate of
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8 discharge from this seep, the close charge balance of the sample water, and the relative clarity of
9
10 the water at the point of discharge.
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15 High nitrate concentrations have been found in other studies of groundwater discharge
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17 wetlands in the northeast (Burns, 1998; West *et al.*, 2001; Burns and Kendall, 2002). McHale *et*
18
19 *al.* (2002) found that high stream water nitrate concentrations coincided with peaks in the
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21 groundwater contribution discharging from till at high topographic positions in the landscape.
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23 However, nitrate concentrations were low in ToB groundwater, likely a result of denitrification
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25 due to reduced conditions, or to uptake by vegetation. Burns (1998) suggests that high nitrate
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27 levels of springs are a result of older groundwater from deep flow paths entering below the
28
29 rooting zone, particularly in areas of bedrock fractures. The extent to which fractures affect
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31 groundwater flow paths in this research area is not known. The area upslope of the seeps contain
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33 thin soils over granite bedrock. The effect of deep groundwater on nitrate concentrations is likely
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35 low given the placement of these sites near the top of the catchment, 185 m away and only seven
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37 meters higher. Furthermore, the ToB nitrate concentrations were not statistically different from
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39 the SGW samples, as only the SGW – SW comparison was significant. This indicates
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41 contributions from within the seep itself, or as a result of a mixture of groundwater interacting
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43 with well aerated soils from within the seep. High nitrate concentrations emanating from
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45 biologically active soils have been reported elsewhere, supporting the likelihood of a similar
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47 effect at the study site (Bowden, 1987; Cirimo and McDonnell, 1997). In addition, ¹⁵N values for
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49 these groundwater and surface water samples did not indicate highly enriched (denitrifying)
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3 conditions in ToB or SGW samples as $\delta^{15}\text{NO}_3\text{-N}$ concentrations at these locations were only
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5 slightly enriched ($+10.6 \pm 2.6 \text{ ‰}$ and $+6.3 \pm 0.9 \text{ ‰}$, respectively), whereas seep outflows
6
7 indicated isotopic mixing of these waters ($+8.5 \pm 1.5 \text{ ‰}$) (Morley, unpublished data).
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10 Corresponding stream-water values at Dutton Creek ($< +2 \text{ ‰}$) are lower than concentrations
11
12 found in similar northeastern streams, which average approximately $+5 \text{ ‰}$ (Mayer *et al.*, 2002).
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15 We therefore feel that these groundwater slope wetlands, during the growing season, provide a
16
17 constant source of cooler groundwater, readily available for mineralization and nitrification by
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19 the large organic soil layer at these seepage wetland sites. We did not observe an increase in
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21 stream water nitrate concentration such as those found in groundwater discharge areas in near-
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23 stream environments (i.e., Angier and McCarty, 2008) as we believe the longitudinal length from
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25 seep outflow to the stream (over 100 m) at the study site likely consumes the relatively high
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27 nitrate levels at seep outflows such that it does not affect stream-water chemistry (Simon *et al.*,
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29 2010).
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34 35 CONCLUSIONS

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38 This study demonstrates that water forming headwater seepage areas in our study area in
39
40 eastern Maine is influenced by shallow groundwater, and provides important hydrological
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42 functions to headwater regions. The primary function is the sustenance of surface water flows to
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44 headwater streams during periods of low flow. The effects of this in our study are two-fold. First,
45
46 it extends aquatic habitat for wetland-dependent biota farther into headwater reaches, and
47
48 secondly it maintains water flow during a period when water levels and temperatures could
49
50 threaten survival of aquatic organisms. This has important consequences for headwater stream
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52 biota including sustenance of freshwater fisheries (Labbe and Fausch, 2000), stream
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54 invertebrates (Collins *et al.*, 2007; Orendt, 2000), vegetation communities (Hall *et al.*, 2001), and
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3 amphibian populations (Gomi *et al.*, 2002; Morley, 2008). We found that groundwater flow
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5 paths in headwaters can be concentrated into relatively small areas, such as in seeps, which if
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7 located high in the catchment can contribute up to 80% of runoff during base flow periods. Due
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9 to the emergence of this subsurface water, seeps also provide a source of base cations and
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11 alkalinity to surface waters thereby buffering downstream systems from acidic conditions
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13 common during precipitation events. These base cations can help maintain cation exchange
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15 saturation and allow resorption of exchangeable base cations onto exchange sites farther
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17 downstream. This is important for streams with low acid neutralizing capacity, as is common in
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19 headwaters regions. The concentrated groundwater discharge at the head of these wetlands
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21 results in increased surface water discharge and ion contributions to the first order stream.
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23 However, the results of this study are conservative because our seeps were located approximately
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25 100 m from the stream. Seeps located closer to surface water bodies would increase stream flow
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27 and ion contribution more than those in this study.
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35 The cumulative effect of headwater wetlands in similar hydrologic landscapes may be
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37 substantial considering estimates of headwater streams in the United States and Europe range
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39 from 50 to over 75% of total stream length (Leopold *et al.*, 1964; Krecek and Haigh, 2006;
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41 Nadeau and Rains, 2007). Seeps in headwaters regions function to increase the length of the
42
43 aquatic environment in the landscape, and increase the duration of surface water supply to these
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45 streams while buffering stream water chemistry.
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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	

TOB = Top of Bedrock (piezometer installed to bedrock interface)

SGW = Shallow groundwater (installed at 0.6 m below ground surface)

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

Site*	Drainage Area (m ²)	Total Area (%)	Mean Discharge (m ³ /sec)	Mean Runoff (mm/hr)	Range (mm/hr)
AS1	72787	52	3.7 x 10 ⁻²	1.85	0.14 – 3.56
BS1	55472	39	8.0 x 10 ⁻²	5.19	1.85 – 8.52
HW1 and HW2	12627	9	4.1 x 10 ⁻²	26.48	12.26 – 40.69

* = Refer to Figure 1.

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TABLE 3. Summary of Ion Chemistry. Data organized by water depth and wetland/upland location for all piezometers in the 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	11.1	2.3	3.1	0.6	0.5	4.1	0.2	27.0	7.1	1.3	0.4	
		(SD)	(6.6)	(1.2)	(1.6)	(0.4)	(0.2)	(3.3)	(0.3)	(52.7)	(9.3)	(0.3)	(0.6)	
	Seep	N	6	8	8	8	8	8	8	8	8	8	8	8
		Mean	18.4	6.7	2.6	0.8	1.4	4.9	0.1	25.3	3.9	0.8	0.4	
		(SD)	(22.4)	(3.5)	(1.0)	(0.2)	(0.8)	(3.1)	(0.1)	(33.3)	(1.7)	(0.6)	(0.2)	
	Toe	N	7	15	15	15	15	15	15	15	15	15	15	15
		Mean	20.1	5.9	5.0	3.8	1.4	4.6	0.1	13.1	12.6	1.4	0.5	
		(SD)	(8.1)	(2.8)	(9.3)	(12.3)	(0.6)	(1.1)	(0.2)	(8.6)	(11.5)	(2.0)	(0.3)	
	Bench	N	5	5	5	5	5	5	5	5	5	5	5	5
		Mean	12.0	2.2	2.3	0.5	0.5	5.3	0.2	2.1	2.3	1.1	0.4	
		(SD)	(18.9)	(0.9)	(0.3)	(0.3)	(0.2)	(93.7)	(0.3)	(1.7)	(0.9)	(0.5)	(0.3)	
SGW	Upland	N	3	4	4	4	4	4	4	4	4	4	4	
		Mean	5.6	1.6	1.7	0.4	0.3	3.1	<0.1	8.9	2.9	1.3	0.3	
		(SD)	(1.0)	(0.4)	(0.3)	(0.1)	(0.1)	(2.0)	(<0.1)	(4.7)	(2.6)	(0.1)	(0.3)	
	Seep	N	19	26	26	26	26	26	25	26	25	26	25	
		Mean	11.8	4.2	2.4	0.7	0.6	5.0	0.1	19.3	5.5	0.9	0.3	
		(SD)	(8.0)	(3.6)	(1.2)	(0.5)	(0.6)	(7.5)	(0.1)	(21.6)	(5.5)	(0.5)	(0.2)	
	Toe	N	15	32	32	32	32	32	32	32	32	32	32	
		Mean	16.2	4.6	2.8	1.5	0.9	6.2	0.7	6.8	7.8	0.5	1.0	
		(SD)	(9.5)	(2.2)	(2.7)	(4.2)	(0.4)	(5.2)	90.5	(5.4)	(3.8)	(0.8)	(0.4)	
	Bench	N	12	12	12	12	12	12	12	12	12	12	12	
		Mean	4.3	1.2	2.5	1.0	0.2	2.1	<0.1	2.0	2.2	1.5	0.2	
		(SD)	(3.9)	(0.4)	(2.2)	(2.6)	(0.1)	(0.5)	(<0.1)	(1.7)	(2.3)	(0.5)	(0.1)	
Surface	Stream	N	25	28	28	28	28	28	28	28	28	28	25	
		Mean	5.5	2.3	1.6	0.2	0.5	2.3	<0.1	19.7	2.0	1.1	0.2	
		(SD)	(3.6)	(0.9)	(0.1)	(0.1)	(0.1)	(0.5)	(<0.1)	(30.0)	(0.9)	(0.2)	(0.1)	
	Seep	N	24	27	27	27	27	27	27	27	27	27	26	
		Mean	6.9	2.9	1.5	0.3	0.4	2.3	<0.1	64.4	4.1	1.3	0.2	
		(SD)	(3.2)	(0.6)	(0.1)	(0.1)	(0.1)	(0.4)	(<0.1)	(52.2)	(5.8)	(0.1)	(0.1)	

† 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

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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		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

Lower case superscripts indicate significant difference between seeps; uppercase indicate significant difference above and below seep outflow. Wilcoxon test (p < 0.05). ND = non-detect

LIST OF FIGURES

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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 3m); and surface-water sampling overview (c, not to scale). Note: Stream surface-water sampling sites are white and black dots, while wetlands and wetland surface water sampling sites are in grey. AS = Above Seep, BS = Below Seep, triangles = piezometer locations, circles = surface water collection points.

FIGURE 2. Seep HW1 Groundwater Hydrograph and Weir Stage Response to Precipitation Events in 2005. Precipitation (a) are daily totals, groundwater (b) and weir stage (c) data were recorded at ten-minute intervals. Precipitation data taken from the Bear Brook Watershed Maine research catchment, 21 km east of the study site.

FIGURE 3. Groundwater Head at Seepage Head and Outflow of Seep HW1. Data show top of bedrock (ToB) (0.7-2.5m) 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-notch weirs during base flow in 2004 (a) and 2005 (b).

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.

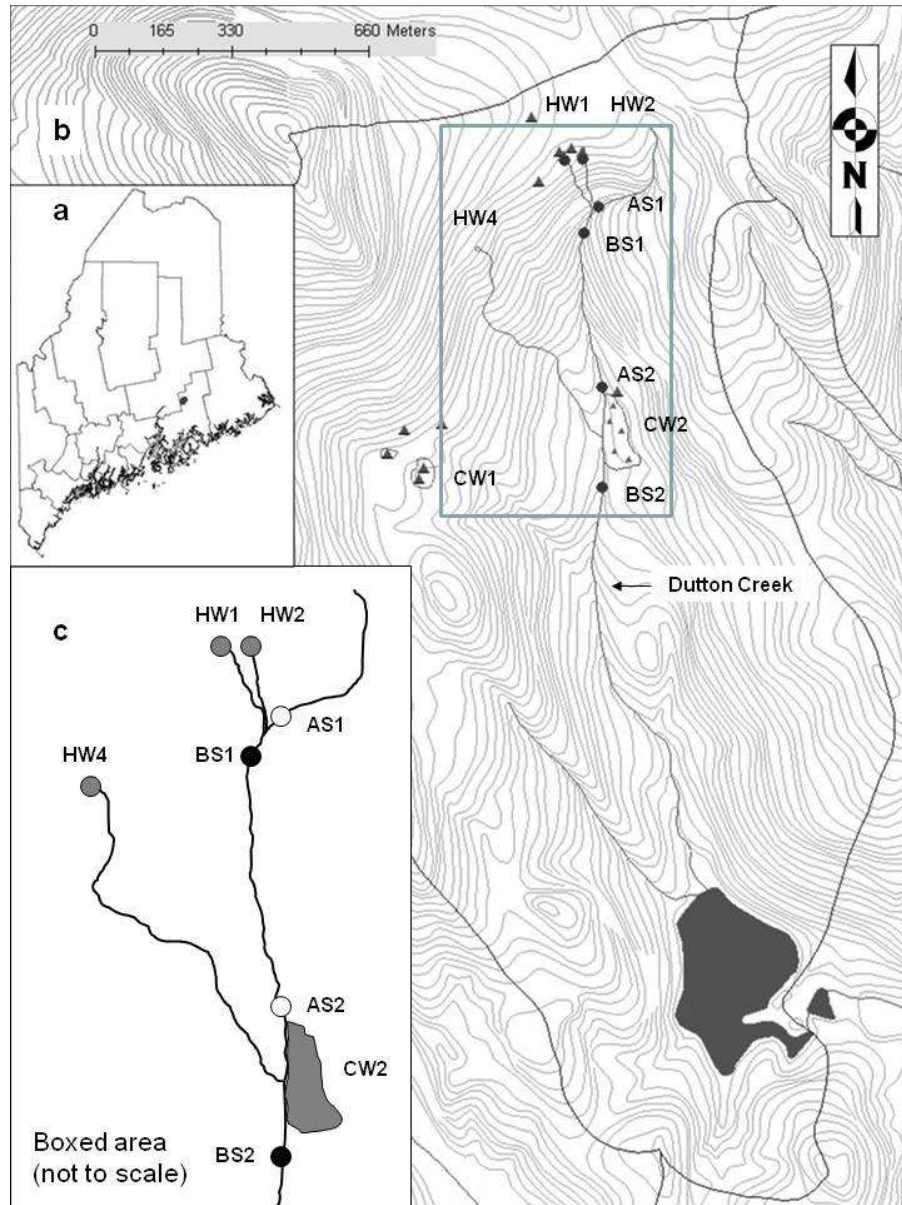


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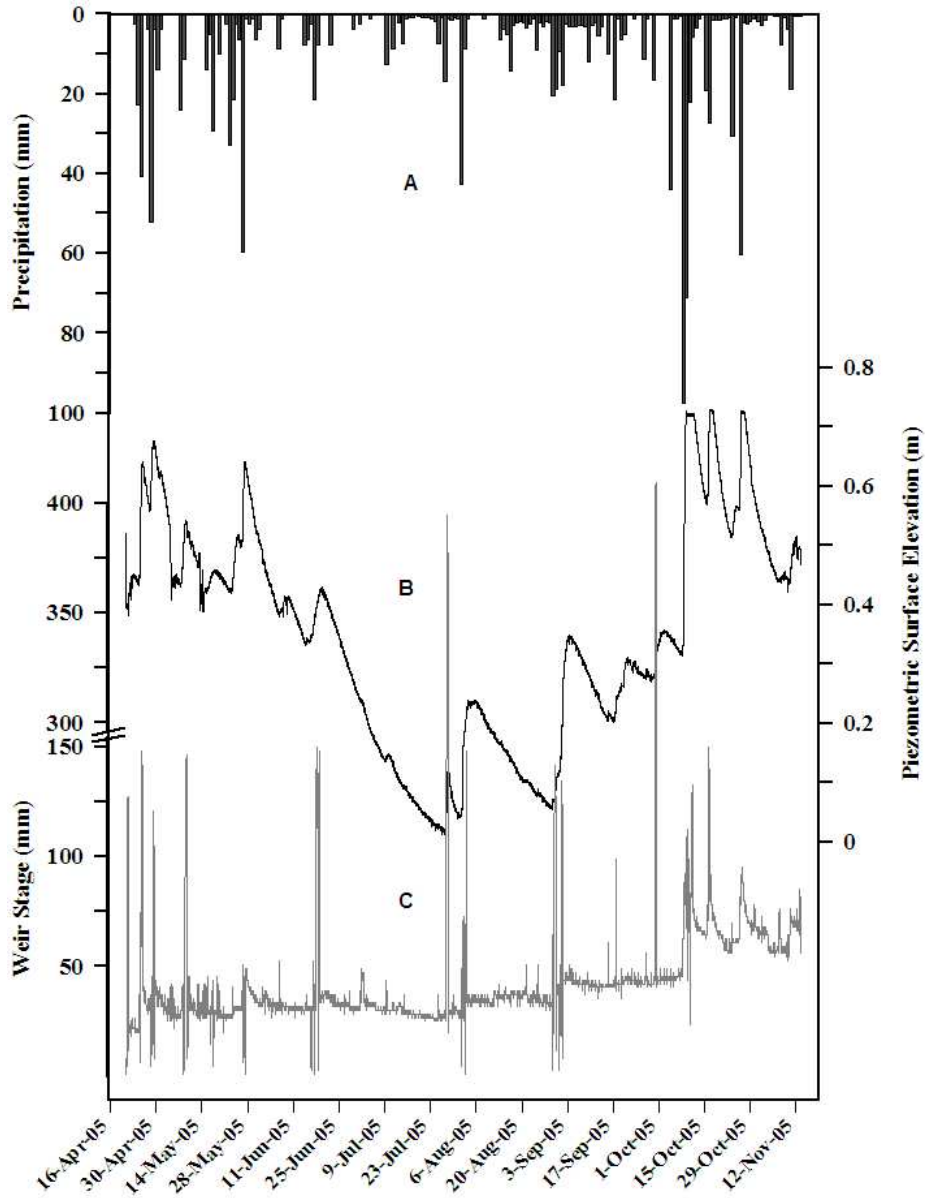


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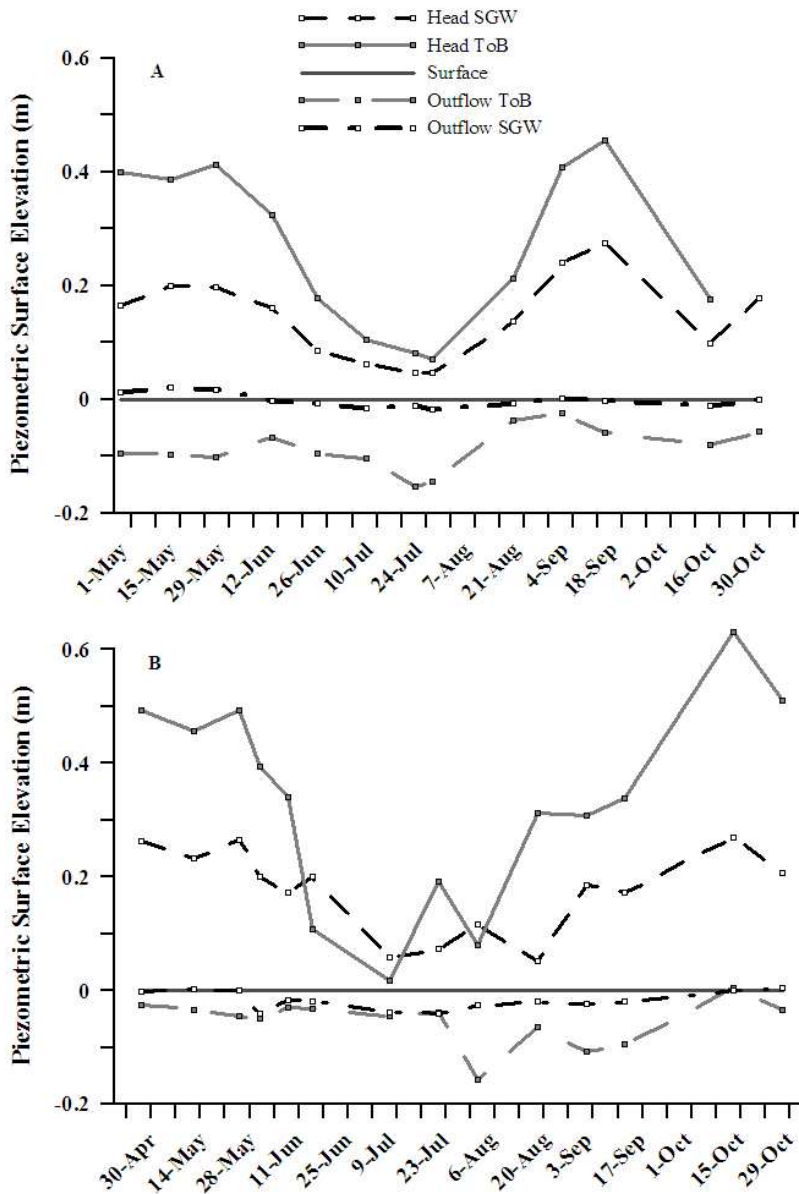


FIGURE 3. Groundwater Head at Seepage Head and Outflow of Seep HW1. Data show top of bedrock (ToB) (0.7-2.5m) and shallow (0.6 m) piezometers at the seep head and seep outflow in 2004 (a) and 2005 (b).
174x259mm (96 x 96 DPI)

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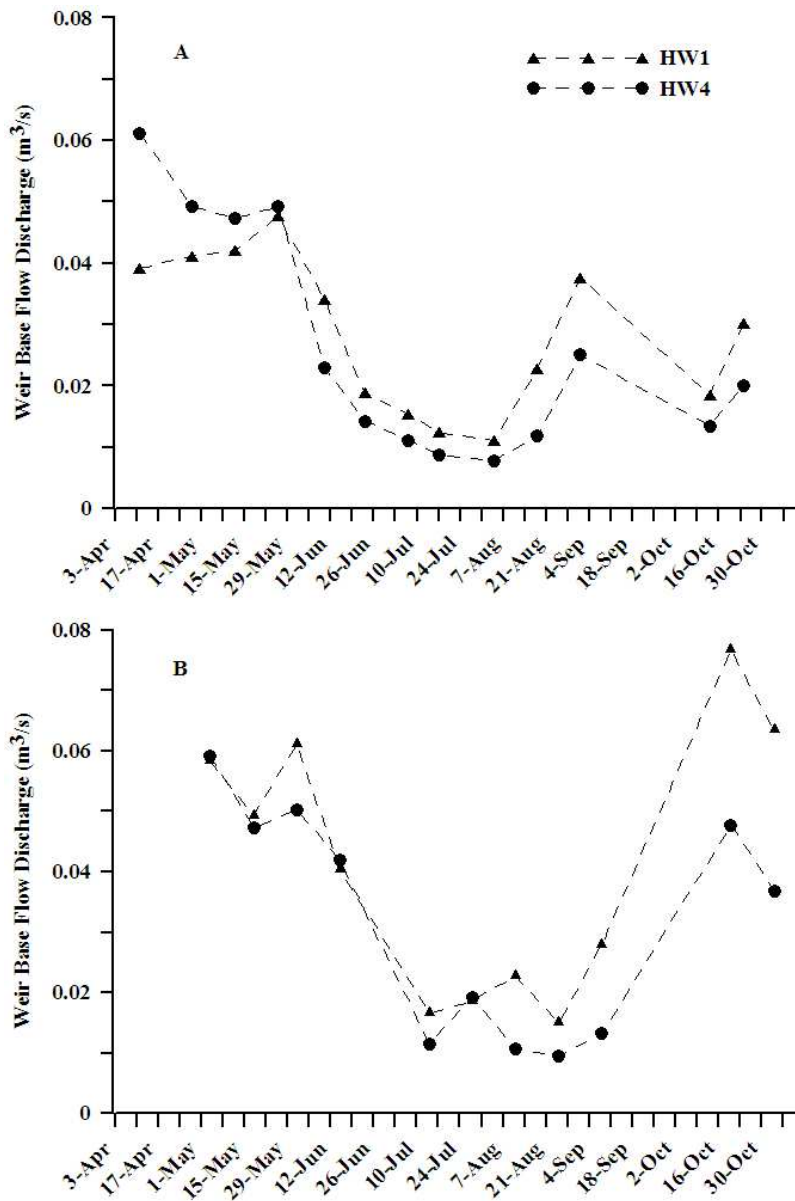


FIGURE 4. Seasonal Trend of Surface Water Discharge From Wetlands HW1 and HW4. Data measured at 90° v-notch weirs during base flow in 2004 (a) and 2005 (b). 177x265mm (96 x 96 DPI)

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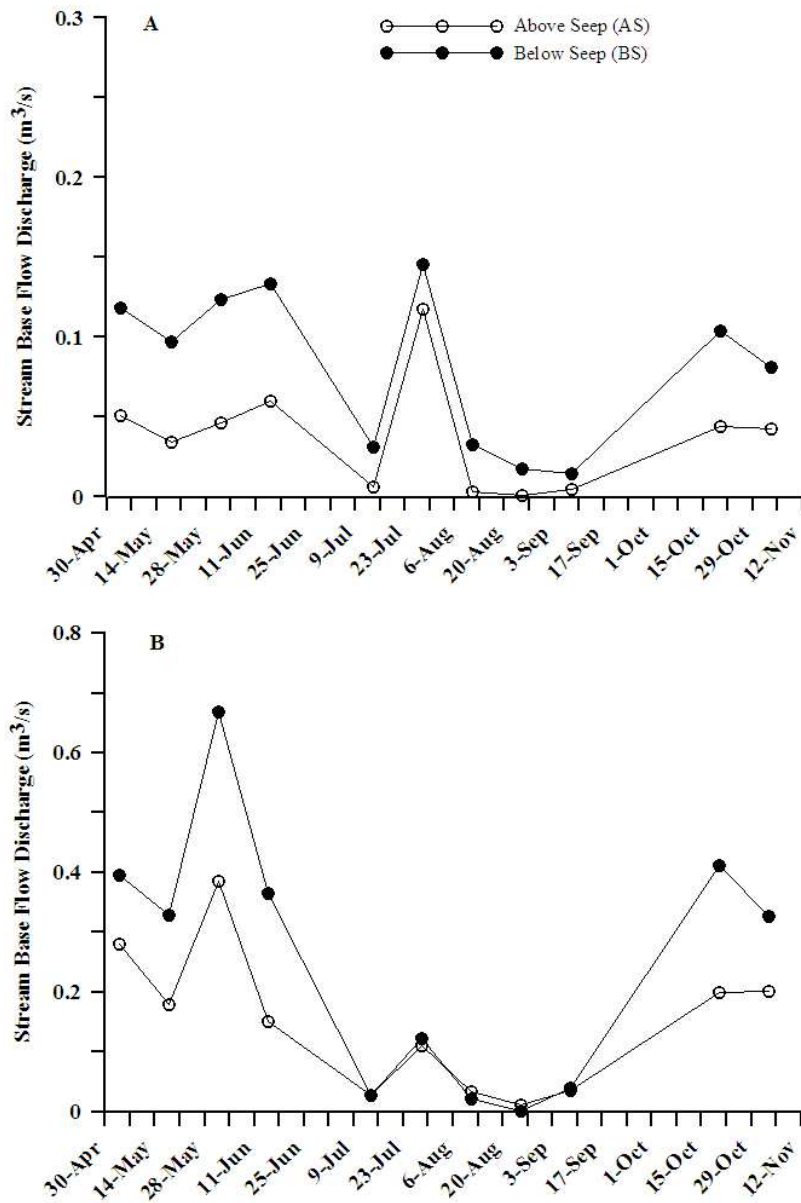


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197x262mm (96 x 96 DPI)

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