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The role of snowmelt and spring rainfall in inorganic nutrient fluxes from a large temperate watershed, the Androscoggin River basin (Maine and New Hampshire)

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Abstract. The importance of snowmelt and spring rainfall to water and nutrient exports from macro-scale watersheds (>1000 km^2) is not well established. Data collected from the Androscoggin River watershed (Maine and New Hampshire) between February 1999 and March 2002 show that the 90-day spring melt period accounted for 39–57% of total annual discharge and is likely driven both by snowpack melting and spring rainfall. While large loads of dissolved inorganic nitrogen (DIN) are delivered to the watershed from snowmelt and rain (from 1.16×10^6 to 1.61×10^6 kg N over the study years), only one third of this N load is exported from the basin during the snowmelt period (0.40×10^6–0.48×10^6 kg N). Despite reduced residence time and temperature limitations on biological N retention, there is a poor mass balance between DIN input to the watershed and the nitrogen exported from mouth of the river. Inferences from a geochemical hydrograph separation suggests that approximately 51–63% of the water leaving the mouth of the Androscoggin river is from these 'new' water sources (rain and snowmelt) while 37–49% is from DIN depleted soil and groundwater. Mixing of water from different sources, as well as nutrient retention by dams in the upper watershed, may account for the large discrepancy between DIN inputs and exports from this watershed.

Introduction

Several large-scale studies have quantified the annual inputs and exports of nitrogen (N) to and from watersheds along the eastern coast of the United States (Boyer et al. 2002; Mayer et al. 2002; Seitzinger et al. 2002; Van Breemen et al. 2002). While annual budgets are important, they may mask important seasonal and intra-annual processes that strongly influence N dynamics in both the watershed and downstream coastal waters. In seasonally snow-covered regions, such as the Androscoggin River watershed in northern New England, most precipitation falling on the basin during the winter is held above ground in the snowpack and then released over a relatively short time during snowmelt (Rascher et al. 1987). Thus, the greatest delivery of nitrogen to downstream coastal ecosystems often occurs during a brief period of spring snowmelt, when nitrogen-rich water from the snowpack is released (Rascher et al. 1987).

Anthropogenic emissions of N to the atmosphere have increased steadily in recent decades (Vitousek et al. 1997; Lefer and Talbot 1999), resulting in increased wet and dry atmospheric deposition to terrestrial and aquatic ecosystems (Ollinger et al. 2002). The deposition of anthropogenic N from industrial sources was shown to be a primary predictor of riverine nitrogen export in the Northeastern United States (Howarth et al. 1996). These deposits of atmospheric N from anthropogenic sources may most heavily influence ecological processes in riverine and estuarine waters during the spring season, when the winter snowpack melts and runoff and productivity are high. The influence of anthropogenic N inputs upon the adjacent Kennebec River N levels has been demonstrated by correlation to upstream population density, while industrial point-source N inputs were cited in the Androscoggin River (Hunt et al. 2005). These point sources contribute a seasonally consistent nutrient source to the Androscoggin River and coastal waters.

An assessment of the importance of seasonal snowpack storage and delivery of runoff and dissolved inorganic nitrogen (DIN) is of particular interest in this river basin, as the timing of peak discharge from this river has been correlated with the occurrence of harmful algal blooms in the Gulf of Maine (Anderson 1997).

Extensive research has been conducted to determine snowmelt water pathways and the sources and fate of nitrogen during transport in fluvial systems. Factors such as topography, snowpack depth, ground frost, rainfall, air temperature, and antecedent moisture affect the flowpaths of water and N deposition from the snowpack (Creed et al. 1996; Shanley and Chalmers 1999; Shanley et al. 2002). However, modeled runoff generation from large watersheds is typically influenced by the spatial and temporal distribution of precipitation and runoff routing, rather than the small-scale variability in soil type and land use important in smaller catchments (Uhlenbrook et al. 2004). Most snowmelt studies have focused on small and meso-scale watersheds (Rascher et al. 1987; Hornbeck et al. 1997; Shanley and Chalmers 1999; Shanley et al. 2002), with little or no work on snowmelt fluxes from macro-scale watersheds despite a proportionally higher impact on coastal ecosystems. We define the scales as small (<10 km^2), meso-scale (>100–1000 km^2), and macro-scale (>1000 km^2) as noted in Soulsby et al. (2004) and Uhlenbrook et al. (2004). Here we report the contributions of snowpack meltwater and spring rainfall to DIN fluxes from the macro-scale Androscoggin River Basin to the nearshore Gulf of Maine for the four spring freshets from 1999 to 2002. We use these results and estimates of runoff sources to draw inferences about the retention and export of DIN in a large river network during high flow spring snowmelt periods.

Materials and methods

Study area

The Androscoggin River basin is located in Maine and New Hampshire and drains a total area of 9127 km^2 along its 259 km length (Figure 1). The river flows through a largely forested watershed (85%), with a relatively small fraction of urban and agricultural land (6%). The geology of the river basin is till-covered bedrock with narrow valleys of stratified drift and some fine-grained marine deposits in the southern portions (Montgomery 2002).

Six dams are located in the upper reaches of the Androscoggin River and are operated for flow management and hydroelectric power generation. The drainage area above the dams represents about 2700 km^2, or 30% of the total upstream watershed study area. The total storage capacity of the reservoirs above the dams is 8.2×10^8 m^3 and they have a combined residence time of approximately 125 days (R. Bouchard, personal communication). Reservoirs are generally drawn down during the late winter to 25–45% of their full storage capacity, in anticipation of the spring snowmelt period. The water accumulated through the snowmelt period is then released over the typical low-flow periods of summer and fall.

Hydrologic data

Snowpack water volume data from approximately 90 stations in Maine were collected by the Maine Cooperative Snow Survey Program (http://www.state.me.us/mema/weather/snow.htm) and used to spatially interpolate snow water equivalent (SWE) using the method of Shepard (1968). We used the date with the maximum volume of water stored in the snowpack just prior to snowmelt to define our snowmelt period. The snowmelt period began 2 weeks before the maximum snowpack, and lasted for 76 days after this date. This 90-day period captured the rising hydrograph just prior to maximum snowpack and encompassed the peak spring discharge for all 4 years while maintaining a consistent window of time to view the snowmelt period among years (Figure 2).

Daily precipitation inputs across the Androscoggin basin were estimated by interpolating between National Climatic Data Center (NCDC, http://www.ncdc.noaa.gov/oa/ncdc.html) precipitation monitoring

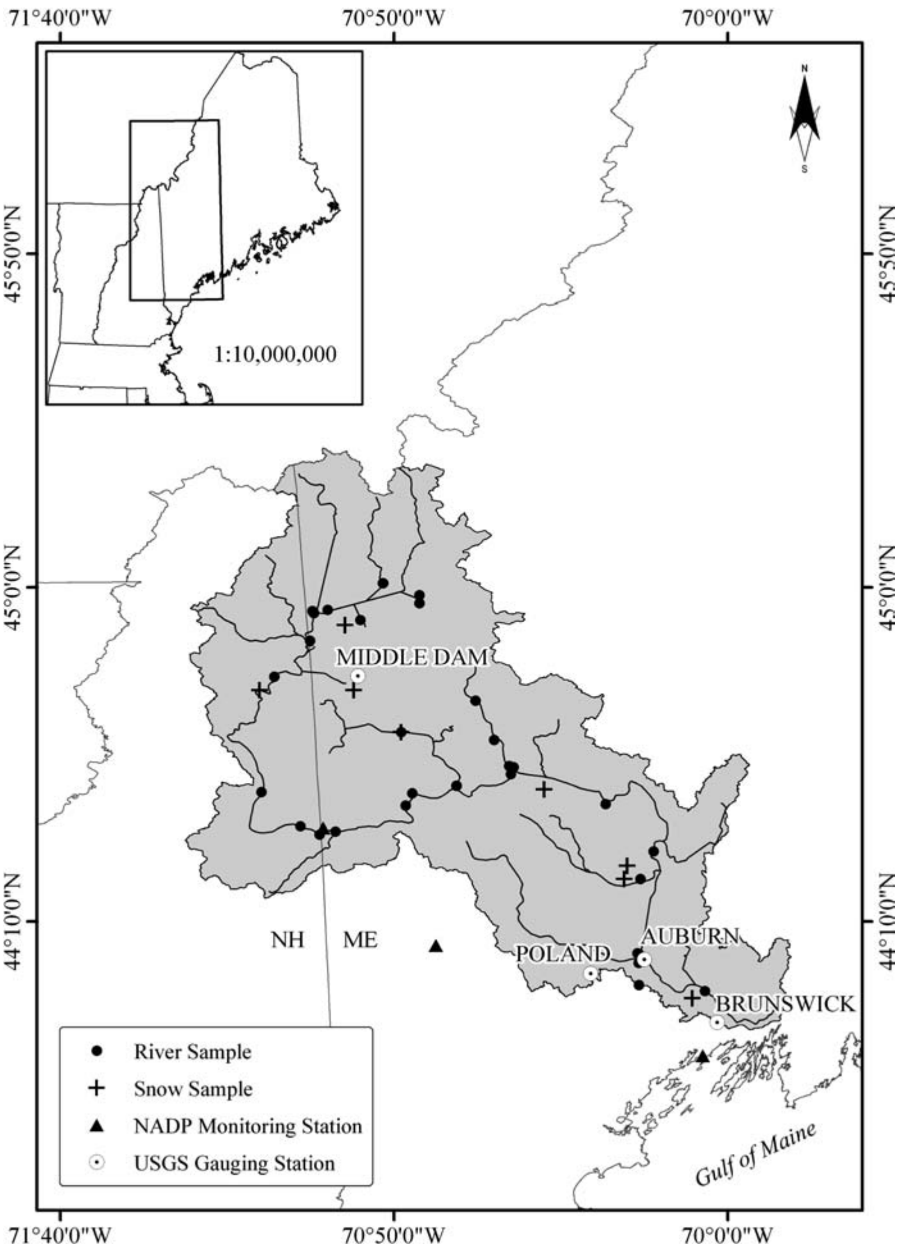

Figure 1. Map of Androscoggin River showing both the snow and river sampling locations. Sixteen sites outside of the watershed were used for the spatial interpolation of the snowpack chemistry, but are not shown on the map to allow for greater detail of the watershed.

stations (Shepard 1968). These daily values were then summed to determine a seasonal spring precipitation volume that fell during the snowmelt period.

Daily flow data for the Androscoggin River were obtained from the US Geological Survey (USGS) gauge at Auburn, ME (entire upstream basin area = 8450 km^2, http://water.usgs.gov/). Winter baseflow was estimated to roughly separate spring event flow from non-event flow at this USGS gauge. Baseflow was defined as the lowest daily discharge recorded at the beginning of the snowmelt period. Baseflow volume was then subtracted from daily discharges over the 90-day spring snowmelt period to separate event flow during the snowmelt period (Figure 2). Based on velocity measurements made by the USGS, the

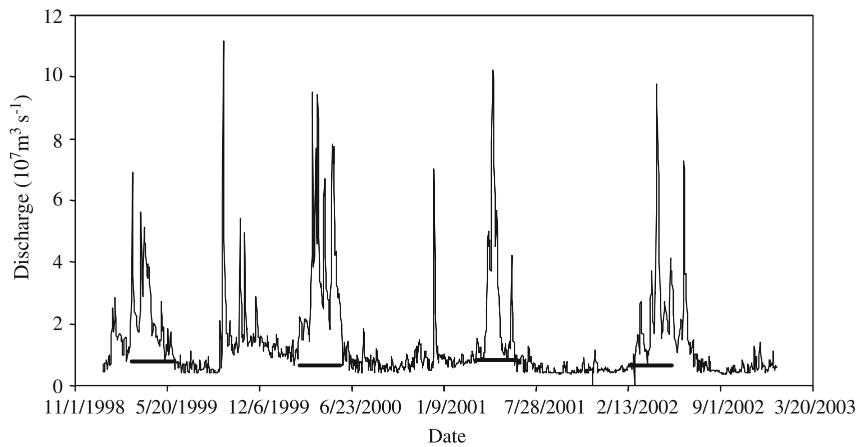

Figure 2. Four-year hydrograph of the Androscoggin River. Flat lines represent the estimated baseflow over the 90-day snowmelt period for each year. Peaks in 2002 not covered by the baseline are the result of large rainfall events.

residence time of the main stem of the Androscoggin is approximately 1–3 days. Some monthly groundwater data were obtained from the USGS (http://waterdata.usgs.gov/nwis/gw) for two locations in the Androscoggin watershed, Brunswick and Middle Dam, during the study period. Also, some discrete groundwater DIN concentration measurements for a monitoring station in Poland, ME were used.

Nutrient sample collection and analysis

Snowpack samples were collected from vertical cross-sections of snowpit profiles at eight sites in and 16 around the Androscoggin watershed on eight trips between February 1999 and March 2002 (Figure 1). Sampling locations were open to direct precipitation and at least 100 m away from roads. One vertical side of a snow pit dug into the ground surface was smoothed, and a square core was removed in sections using a metal spatula. Samples were homogenized and a 500 ml portion of snow sample was stored in an acid-washed HDPE bottle and preserved with approximately 1 ml of sodium azide to inhibit biological activity. Samples were filtered in the lab through a Millipore-HA 0.45 μm filter and frozen until nutrient analysis. Nutrient concentrations from the month of maximum snowpack were spatially interpolated across the basin, again using the method of Shepard (1968). Both the SWE and nutrient fields were then multiplied together to get a total DIN load. Further, all of the spatial and temporal nutrient data for the snowpack DIN concentrations for each year were averaged together to determine a mean snowpack concentration.

The N concentration of rain was estimated using chemistry data from three National Trends Network sites within and in close proximity to the basin (NADP website http://nadp.sws.uiuc.edu/). The total precipitation volume occurring over each snowmelt period was combined with the volume-weighted mean precipitation DIN concentrations from all three stations during the runoff period to obtain a total DIN load. As there were so few data points, a spatial interpolation was not performed on the nutrient data.

River water samples were collected from 28 sites during 20 approximately monthly sampling trips between February 1999 and April 2002. Further intensive river sampling (e.g., 1–7 day sampling intervals) was conducted at Brunswick, ME near the mouth of the Androscoggin River in 1999, 2001, and 2002 to measure temporal variability. Daily DIN concentrations at Brunswick were estimated by linearly interpolating between sampling dates. Daily discharge was multiplied by daily DIN concentration estimates and summed to determine a snowmelt-period nutrient export.

Surface water grab samples were collected from a bridge near the middle of the river channel using a plastic bucket rinsed with river water. Samples were stored in acid-washed 125-ml HDPE bottles, preserved with approximately 1 ml of chloroform or sodium azide, and stored at 4 °C until analysis. A comparison study has shown no difference in nutrient concentration as a result of preservative used (Loder, unpublished data).

All samples were analyzed for nitrate (NO_3), nitrite (NO_2), ammonium (NH_4), and silicate (SiO_4) by flow injection using a Lachat QuikChem 8000 Automated Analyzer (Milwaukee, WI). Nitrate was the major nitrogen species, and there was virtually no nitrite in these samples. Dissolved inorganic nitrogen was calculated as the sum of nitrate, nitrite, and ammonium. Instrument detection limits were 1.0 μM for NO_3, 0.3 μM for NH_4, and 0.01 μM for SiO_4.

Geochemical hydrograph separation

A two-component mass balance model using snowpack and riverine Si concentrations was used to estimate the contributions of 'new water' (snowmelt and spring rainfall) and 'old water' (groundwater and soil water) to total discharge via the following set of equations:

$$Q_r = Q_o + Q_n \tag{1}$$

$$Q_r C_r = Q_o C_o + Q_n C_n \tag{2}$$

$$Q_o = Q_r C_r / C_o \tag{3}$$

where Q is discharge, C is the tracer (Si) concentration, r, o, and n stand for river discharge, 'old' water, and 'new' water, respectively, and the concentration of Si (C_n) in the new water is essentially zero. The applications of these equations to this study are subject to assumptions described by Sklash and Farvolden (1979) and Laudon and Slaymaker (1997). Briefly, these assumptions include the use of a single value to characterize Si in snowmelt and groundwater (or that the variations can be documented), that these concentrations are significantly different, and that contributions from additional components are negligible. Winter river samples collected at the mouth of the Androscoggin prior to snowmelt (December–February) are assumed to be dominated by discharge of pre-event subsurface water and are therefore used to characterize 'old' water in our mixing model. 'New' water Si concentrations (C_n) are based on the collected snowpack samples. The uncertainty of the mixing fractions of 'new' and 'old' water was estimated using the approach of Genereux (1998), where the uncertainty in mixing is related to the mean concentration and associated uncertainty of each water source.

Results

Inputs of snow and rain

While snowpack covered the entire basin prior to melt in all of the years examined, the 2001 snowpack had a much greater water content than the other 3 years (Table 1). The 2001 snowpack also lasted longer, with maximum snowpack depth determined to be 2 weeks to a month later than the other 3 years.

The total volume of water from rain and melt during the 90-day period ranged from 2.57×10^9 to 4.11×10^9 m^3. These values are the same order of magnitude as the volume of water measured leaving the basins during the snowmelt period, ranging from 2.14×10^9 to 3.44×10^9 m^3 (Table 1). Thus, it appears that a similar volume of water entering the hydrologic system in the spring also left the system during the same time frame. However, the volume of water retained by the upstream reservoirs is not insignificant, ranging from 3.6×10^8 to 5.7×10^8 m^3, or 8 to 15% of the total water input (Table 1). While the relative contribution of spring rainfall and snowmelt to river discharge are not explicitly known, spring rain may be a significant source of runoff. For example, rainfall accounted for 53–75% of the total 'new' water input in 1999, 2000 and 2002, but only 33% in 2001, characterized by a large snowpack and spring drought conditions (Table 1).

Table 1. The interannual variability of both snowpack and precipitation water and nutrient characteristics are shown for the four study years, including a summary of mean measured DIN concentrations in μM l^{-1} in the Androscoggin Basins' snowpack as well as at the Androscoggin River mouth.

Year	1999	2000	2001	2002
Date of maximum snowpack	3/16	3/13	4/2	3/3
Snowpack				
SWE (m)	0.14	0.12	0.31	0.1
Watershed snowpack water volume (10^9 m^3)	1.22	1.06	2.68	0.87
Mean seasonal snowpack DIN concentration (μM)	23.3	28.6	22.6	31.2
Standard deviation	5.93	12.8	8.1	11.4
Number of samples	7	13	27	13
Maximum snowpack DIN storage (kg km^{-2})	38	41	112	36
Maximum snowpack DIN load (10^5 kg DIN)	3.31	3.52	9.66	3.15
Precipitation				
Volume of new precipitation over snowmelt (10^9 m^3)	1.35	3.05	1.34	2.57
DIN in precipitation over snowmelt period (10^5 kg DIN)	8.25	12.56	5.19	10.05
Total input volume as wet precipitation (%)	53	74	33	75
Total DIN input as wet precipitation (%)	71	78	35	76
Reservoirs				
Estimated input volume retained by reservoirs (10^8 m^3)	3.6	3.9	4.8	5.7
Total input volume retained by reservoirs (%)	11	8	10	15
River				
Annual Discharge (10^9 m^3)	5.81	6.01	4.07	4.46
Snowmelt period discharge (10^9 m^3)	2.25	3.44	2.34	2.14
Fraction exported during snowmelt (%)	39	57	57	48
Mean measured river DIN concentration (μM)	12.7		16.9	14.9
Standard deviation	2.3		6.4	14.9
Number of samples	35		30	18

The maximum SWE, water volume, DIN load, and storage in the snowpack as well as the total volume and total N load in precipitation falling during the spring runoff period on the Androscoggin River Basin are also described. The percent water volume and DIN load that precipitation comprises as a fraction of the total inputs from precipitation and snow is also listed. Also listed are annual discharge, discharge during the snowmelt period, and fraction of annual discharge exported during our defined snowmelt period. The snowmelt period discharge listed below includes both base and event flow.

Our Si hydrograph separation indicated that spring rainfall and snowmelt contributed approximately 63% (±7% at the 75% confidence intervals) and 51% (± 3%) of the total discharge from the mouth of the Androscoggin River during the defined snowmelt periods in 2001 and 2002 respectively (early March to the end of May, Figure 3). This translates into surface water contributions of approximately 1.1×10^9 m^3 per year to this basin. Snowpack Si concentrations were much lower (range = 0.1–0.6 μM) than pre-event Si concentration in the river water (range = 69.2–81.3 μM), reducing the uncertainty in our results.

Snowmelt period water budget

Our snowmelt period water budget included inputs of snowpack water and spring precipitation, riverine output, and changes in reservoir storage (Figure 4). Inputs in 1999 and 2000 roughly equaled outputs plus reservoir storage, suggesting evapotranspiration during the snowmelt period and changes in total groundwater storage were relatively small. In contrast, in 2001, greater water input than river discharge plus reservoir storage likely reflects a larger snowpack and a drier spring than the other 3 years. Greater inputs than export also occurred in 2002, though to a lesser degree. Monthly water table depths were plotted for two locations in the watershed that had complete data for the four study years (Figure 5). At both the Middle Dam and Brunswick sites, the latter 2 years (2001 and 2002) had the lowest water table prior to melt.

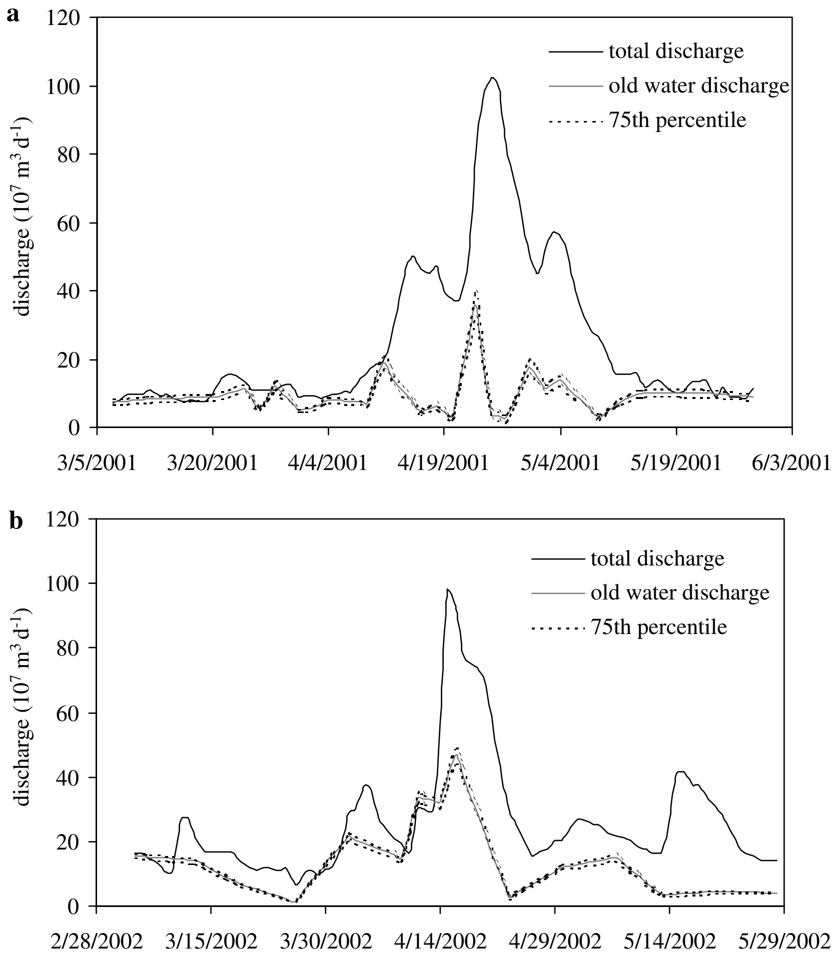

Figure 3. Geochemical hydrograph separations for 2001 (a) and 2002 (b).

Snowpack and rainfall chemistry

While DIN snowpack concentrations did not vary considerably from year to year, the DIN load in the snowpack did vary, reflecting the interannual variation in snowpack water storage, with 2001 having the greatest snowpack storage of DIN (Table 1). DIN was dominantly nitrate, with concentrations typically two to four times higher than ammonium. There was some fluctuation in these DIN data between years and the mean annual DIN concentrations ranged from 22.6 μM (2001) to 31.2 μM (2002) (Table 1). Silica concentrations in the snowpack were typically less than 1.5 μM.

Because spring rain volumes were often greater than snowpack water storage, DIN contributions from rain made up a substantial portion of the total load to the basin during the snowmelt period (Table 1). DIN concentrations in the rain falling in the 90-day spring melt period did not vary markedly from year to year (ranging from 28–51 μM). DIN loading in spring rains ranged from 0.52–1.26 $\times$ 10^6 kg of N during the study period. Nitrogen in the rainfall during the spring melt period was the equivalent of approximately 71–78% of the total precipitation + snowpack DIN input to the rivers, during the melt period, for 1999, 2000, and 2002, but only 35% of the total DIN in 2001.

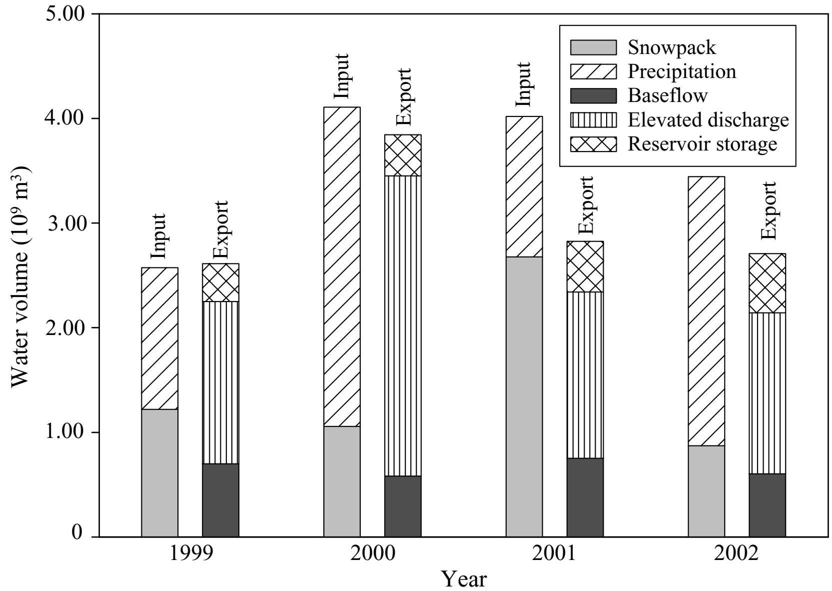

Figure 4. A comparison of total water inputs to and outputs from the Androscoggin River basin during the spring freshet. The volume of water in the maximum snowpack and precipitation over the runoff period are compared to change in reservoir storage (and thus the amount of water retained by the reservoirs) as well as discharge, separated by baseflow and spring runoff, at the mouth of this river.

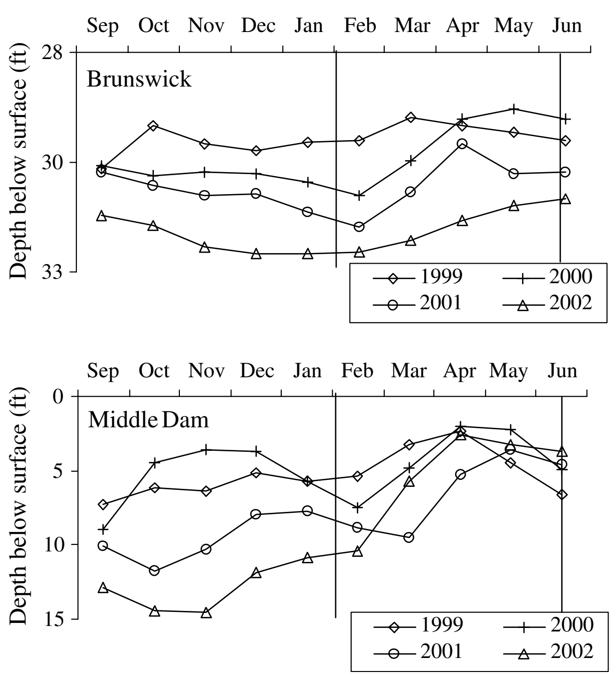

Figure 5. Line graphs showing the depth of the water table below the ground surface (in ft) at two USGS monitoring stations within the Androscoggin Watershed (http://www.waterdata.usgs.gov/nwis/gw). Vertical lines, one between January and February and the other in June, represent the snowmelt period in both plots. The Brunswick Station shown at the top is located near the mouth of the watershed while the Middle Dam Station is located in the northwestern part of the watershed.

River chemistry

The mean DIN concentrations at the Androscoggin River mouth during the runoff period ranged from 12.7 to 16.9 μM during the study years. There was little spatial variability in the seasonal means of the headwater and tributary DIN concentrations. In 2001, a year with high frequency nutrient sampling at the River mouth, approximately 50% of the annual DIN flux occurred during the 3 months of the spring snowmelt period. The annual DIN export from this river for 2001 was estimated to be 9.43×10^5 kg DIN, 4.76×10^5 kg of which was released during snowmelt.

Snowmelt period nitrogen budget

We constructed an inorganic nitrogen budget for the spring melt period for the Androscoggin basin (for 1999, 2001, and 2002), accounting for precipitation inputs via snowmelt and spring rain and exports at the mouth. Total loading ranged from 1.16×10^6 to 1.61×10^6 kg N over the 4 years, with rain DIN dominating inputs in 1999, 2000, and 2002 (Figure 6). High temporal resolution DIN data were not available at the river mouth in 2000. Therefore, DIN export was estimated from one measurement at the mouth and two measurements at the next upstream station. All three of these measurements were taken within four day of each other and thus the grey bar representing DIN export in 2000 is a very rough estimate. Exports at the mouth were remarkably similar (4.03×10^5–4.8×10^5 kg N), despite the variability in the amount and dominant form of loading.

Discussion

In general, the 90-day spring runoff period contributed 39–57% of the annual discharge from the Androscoggin basin. Large quantities of DIN were exported from the river mouth during this high discharge

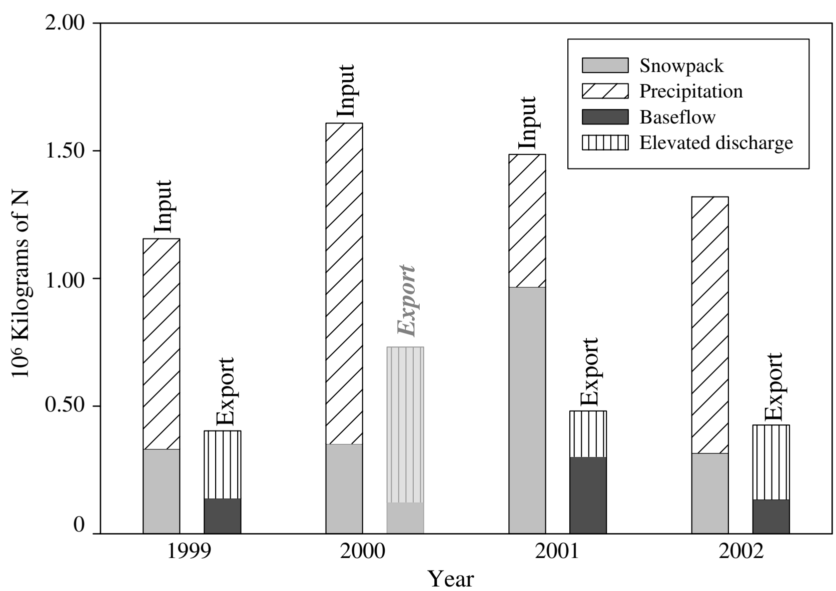

Figure 6. Comparison of N inputs to and exports from the Androscoggin River. Mass of N stored in the maximum snowpack, total N received to the basin via precipitation over the snowmelt period, and total N passing through the river mouth during the snowmelt period, separated as baseflow and runoff. Note that, due to a lack of high resolution N data in 2000, the volume of N exported was roughly estimated from one point measurement at the mouth and two point measurements of DIN concentration taken at the next upstream station. Each of these three measurements were collected within 4 days of one another. Thus, the bar representing export in 2000 is intended to provide only an estimate of the value.

period, contributing half of the annual inorganic nitrogen exported from the watershed in 2001. Further, snow stored during the winter and released during the spring melt period accounted for a large portion of the spring runoff and nutrient export. However, the volume of spring rainfall which fell during this period was an equal, if not greater contributor to water and N export during our study period. This observation is in contrast to the many snowmelt studies conducted in the high elevation catchments of the western and midwestern regions of the United States, such as the Sierra Nevada and the Rocky Mountains, where a greater proportion of the annual precipitation falls as snow than as rain (from 66 to 90%, see Alexander et al. 1985; Sickman et al. 2003).

Prior research in smaller watersheds has shown that microbial processes regulate stream-water nitrogen concentrations (Rascher et al. 1987; Sickman et al. 2003). Work in the Adirondack Mountains of New York led Rascher et al. (1987) to hypothesize that it was mineralization and nitrification in the forest floor that led to an observed five-fold enrichment of nitrate in forest floor leachate over snowpack inputs. Unfortunately, we do not know the effect of shallow subsurface microbial processes in the Androscoggin watershed, which is three orders of magnitude larger than that monitored by Rascher et al. (1987).

Basin inputs from rain and snow during the snowmelt period correspond closely with the volume of water observed leaving the river mouth for 1999 and 2000, but to a lesser extent in 2001 and 2002. The discrepancy between water inputs and exports during these latter 2 years may be explained by relative changes in groundwater storage (Figure 5). While these two stations cannot be used to make conclusive statements about the entire basin, both indicate that groundwater levels prior to snowmelt were lower in 2001 and 2002 than in the other 2 years. Further, the change in groundwater levels during the melt period was large in 2001 at both stations (0.61 m at Brunswick and 1.79 m at Middle Dam) and in 2002 at Middle Dam (2.4 m). Thus, the discrepancies between inputs and outputs of water in the Androscoggin Basin in 2001 and 2002 may be due to a significant volume of groundwater recharge.

While contributions from spring rain and snowmelt varied from year to year, the mass of DIN exported from the river mouth during the freshet was similar in 1999, 2001, and 2002 (Figure 6). In all years there was a great difference between DIN inputs from snow and rain and the amount of DIN exported from the watershed during our 90-day melt period. This study did not include inputs from dry deposition, which have been shown to contribute 10–20% of the total annual deposition in the adjacent Gulf of Maine (Jordan and Talbot 2000) or inputs of dissolved organic nitrogen. Further, anthropogenic inputs to the stream were not assessed and thus, the river removal is likely greater than our estimates. This suggests that watershed nitrogen retention may be high during the snowmelt period, despite cold temperatures and high river network hydraulic loads.

Hunt et al. (2005) reported that DIN concentrations were highly correlated with population density in the Kennebec River watershed in Maine, but found no correlation in the Androscoggin River watershed. In contrast, the primary anthropogenic contributors of DIN to the Androscoggin River were three pulp and paper mills discharging into the river. In August 2001, two of these mills were closed and dramatic drops in Nitrate and Nitrite concentrations were observed in the river network (Hunt et al. 2005). In contrast, we did not see this drop in DIN export during the snowmelt period in the years before and after the mill closures, suggesting that seasonal loading from the snowpack and spring rainfall may mask point source anthropogenic loads to the river.

Approximately 65% less nitrogen was exported from the Androscoggin River basin during snowmelt than is loaded to the watershed via meltwater and rain. While Seitzinger et al. (2002) used a regression model to estimate that 52% of the total annual nitrogen inputs to the Androscoggin River were removed during transport in the river network alone, we found it remarkable to see such a discrepancy between DIN input and export during this high flow period (residence time 1–3 days) when there is presumably minimal uptake by vegetation as water and air temperatures are still so cold (7 and 10 °C respectively at the Auburn gauge, observations from 1966 to 1993, http://www.water.usgs.gov). Total annual nitrogen budgets, sources, and sinks were calculated for this watershed in the early-1990s (see Boyer et al. 2002; Seitzinger et al. 2002; Van Breemen et al. 2002). Results of this work were difficult to compare to this study as we focused only on the inorganic forms of nitrogen during the snowmelt period. However, Boyer et al. (2002)

reported that 69% of the total nitrogen loading to the watershed was stored or lost in the basin annually, similar to the snowmelt period DIN retention of 65% in our study.

Several mechanisms could be invoked to explain the apparent loss or retention of NO_3 released from the snowpack and in spring rainfall. Groundwater recharge could result in the delivery of atmospheric N to soils and groundwater, particularly when preferential flow paths are active and/or biotic activity in the rooting zone is limited (Creed et al. 1996). Other mechanisms include the retention or loss of NO_3 occurring within the aquatic network as well as the biotic retention of NO_3 along surface or shallow subsurface flow paths. However, studies have reported that flow through shallow soils during storm events and snowmelt may also result in the flushing of NO_3 (accumulated from nitrification over the winter), increasing NO_3 fluxes in streams draining temperate forested catchments (Burns and Kendall 2002).

Reservoir storage may also represent a potential nutrient sink, since lakes have been shown to remove significant quantities of N and P (Szilágyi et al. 1990; Jansson et al. 1994; Green et al. 2004; Nixon 2003). Significant volumes of water from spring rain and snowmelt (from 8 to 15%) are retained in the headwaters of this watershed in reservoirs that have an estimated residence time of 125 days (R. Bouchard, pers. comm.). While some have shown that the effect of reservoirs on annual nitrogen removal at the whole basin scale is negligible, it is plausible that if lakes and reservoirs do indeed act as nutrient traps, the retention of spring rain and snowmelt in the headwater reservoirs also traps inorganic nitrogen during the spring freshet (Seitzinger et al. 2002).

Results from our Si hydrograph separation suggest that rainfall and snowmelt accounted for approximately 63 and 51% of the total discharge from the Androscoggin River in 2001 and 2002 respectively (Figure 3). Shanley et al. (2002) reported a scale effect in four nested catchments in the northeastern US, with new water contributions increasing with watershed size (<1–111 km^2, 41–74% new water). These authors hypothesized that with increasing watershed size, the percentage of saturated area and thus the percentage of new water inputs from saturated overland flow also increase (Shanley et al. 2002).

Low DIN groundwater likely represents a significant source of low N drainage water to the Androscoggin River during our study period. Limited USGS groundwater data from Poland, ME in our study catchment ($n = 5$, observed from 2001 to 2003) indicated consistently low NO_3 concentrations (0.43–3.6 μM), suggesting that groundwater DIN concentrations were much lower than those observed in the snowmelt and rain (26–32 μM) and the mouth of the river (13–17 μM). The observed discrepancy in the DIN mass balance calculated for the freshet may be due to mixing of roughly equal contributions of groundwater and 'new' water. This suggests that if low nitrogen groundwater and much higher nitrogen water from rain and snowmelt export similar amounts of water from the Androscoggin River basin during the snowmelt period, then biological processing is minimal.

While it is hard to determine the main factors controlling nitrogen exports in our macro-scale study, our results suggest that the potential impact of climate change on large scale snowmelt dynamics may significant. Groffman et al. (1999) suggest that one of the most significant consequences of global climate change on biotic function and biogeochemical processes in northern forests may be a reduction in snow cover. Frozen soil due to lack of snow cover followed by rainfall would likely lead to high direct surface runoff, particularly during spring rainfall events (Shanley and Chalmers 1999). Changes such as these could have important implications for watershed nutrient dynamics. For example, Mitchell et al. (1996) suggested that regional increases in streamwater nitrate in the northeastern US during the summer of 1990 were caused by widespread soil freezing in December 1989. While not a focus of our study, the role of climate change on snowmelt water and nutrient fluxes from temperate regions deserves further attention.

Conclusions

The melting of the spring snowpack, coupled with spring rains, provides a large source of N to the river basin. However, our results suggest that only half of the water leaving the basin during snowmelt is directly attributable to these sources. We hypothesize that contributions from nitrogen depleted groundwater may account for the poor mass balance of DIN between rain and snowmelt sources and nutrients exported from the river mouth. The operation of man made reservoirs may also play a modest role in nutrient retention. While more than half of the annual fluxes of DIN and water were exported during the freshet, there was still a great deal of inorganic nitrogen from snowmelt and rain lost to groundwater during this high flow period. We hypothesize that as some of this high DIN, low silica melt and rain water becomes groundwater, it exposes the nitrogen to biological uptake and removal, causing the watershed to export less inorganic nitrogen than it receives. Further, biogeochemical processes enrich the groundwater in silica, causing the subsurface contributions to the river discharge to have low DIN, but high silica concentrations. The biogeochemical changes attributable to different water sources are important for understanding how nutrients are discharged to receiving estuarine waters during the freshet.

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