

Effect of reduced winter precipitation and increased temperature on watershed solute flux, 1988–2002, Northern Michigan

R. STOTTLEMYER^{1,*} and D. TOCZYDŁOWSKI²

¹U.S. Geological Survey, 2150 Centre Ave., Bldg. C, Fort Collins, CO 80526, USA; ²Department of Biological Sciences, Michigan Technological University, Houghton, MI 49931, USA; *Author for correspondence (e-mail: robert_stottlemeyer@USGS.gov; phone: +1-970-226-9236; fax: +1-970-226-9298)

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Abstract. Since 1987 we have studied weekly change in winter (December–April) precipitation, snowpack, snowmelt, soil water, and stream water solute flux in a small (176-ha) Northern Michigan watershed vegetated by 65–85 year-old northern hardwoods. Our primary study objective was to quantify the effect of change in winter temperature and precipitation on watershed hydrology and solute flux. During the study winter runoff was correlated with precipitation, and forest soils beneath the snowpack remained unfrozen. Winter air temperature and soil temperature beneath the snowpack increased while precipitation and snowmelt declined. Atmospheric inputs declined for H^+ , NO_3^- , NH_4^+ , dissolved inorganic nitrogen (DIN), and SO_4^{2-} . Replicated plot-level results, which could not be directly extrapolated to the watershed scale, showed 90% of atmospheric DIN input was retained in surface shallow (<15 cm deep) soils while SO_4^{2-} flux increased 70% and dissolved organic carbon (DOC) 30-fold. Most stream water base cation (C_B), HCO_3^- , and Cl^- concentrations declined with increased stream water discharge, K^+ , NO_3^- , and SO_4^{2-} remained unchanged, and DOC and dissolved organic nitrogen (DON) increased. Winter stream water solute outputs declined or were unchanged with time except for NO_3^- and DOC which increased. DOC and DIN outputs were correlated with the percentage of winter runoff and stream discharge that occurred when subsurface flow at the plot-level was shallow (<25 cm beneath Oi). Study results suggest that the percentage of annual runoff occurring as shallow lateral subsurface flow may be a major factor regulating solute outputs and concentrations in snowmelt-dominated ecosystems.

Introduction

Near Lake Superior snowfall can equal half of the annual precipitation (Eichenlaub et al. 1990), and the snowpack may seasonally store up to 50% of annual precipitation (Stottlemeyer and Toczydlowski 1996a, b). Snowmelt can cause sharp changes in stream water chemistry by dilution and solute addition (Johannessen and Henriksen 1978). In this region the extensive snowpack prevents soil freezing which permits forest soil mineralization processes to occur throughout winter (Stottlemeyer and Toczydlowski 1996a). An unfrozen forest floor allows most snowmelt to enter the soil (Typic Haplorthods) where its chemistry is altered (Hazlett et al. 1992). Further chemical alteration

depends on subsurface flowpath and residence time (Rice and Bricker 1995). Should changes in weather patterns or, in time, climate reduce the regional extent or duration of the snowpack or its insulation capacity, the result could prove of greater ecological significance on nutrient flux and below-ground biota than any reasonable scenario for future atmospheric solute inputs (Mitchell et al. 1996; Decker et al. 2003; Fitzhugh et al. 2003). Frozen soils delay snowmelt, can increase the amount of snowmelt solutes directly reaching the stream, and impact soil microbial communities (Biederbeck and Campbell 1971; Pierson and Taylor 1985).

Along the south shore of Lake Superior, since 1950 temperatures have increased and precipitation amounts declined especially in autumn and winter (NOAA 2002). Reduced precipitation and warming temperatures could decrease the spring flux ('flushing') of mobile solutes as dissolved inorganic nitrogen (DIN), organic nitrogen (DON), and dissolved organic carbon (DOC) from forest soils to the stream (Creed and Band 1998; Stottlemeyer and Toczydlowski 1999). Less precipitation might increase the average depth of meltwater flowpath in the forest soil which could further alter ecosystem solute flux (Mulholland et al. 1990; Ross et al. 1994; Battin 1999; Kalbitz et al. 2000). Change in headwater stream hydrology may also alter stream water NH_4^+ nitrification rates and benthic DIN uptake (Peterson et al. 2001).

Reduced precipitation amounts could also lower input of solutes by atmospheric deposition. Solute deposition for the period 1950–1980 is not known, but precipitation concentrations of NO_3^- , SO_4^{2-} , and NH_4^+ appear to have increased (Junge 1958; Junge and Werby 1958; Linsey et al. 1987; NADP 2002). In the Lake Superior Basin during the past two decades inputs of H^+ , NH_4^+ , NO_3^- , and SO_4^{2-} were moderate. The atmospheric deposition of H^+ ($p < 0.01$, $r^2 = 0.32$, $b = -0.004 \text{ kg ha}^{-1} \text{ yr}^{-1}$) and SO_4^{2-} ($p < 0.05$, $r^2 = 0.27$, $b = -0.25 \text{ kg ha}^{-1} \text{ yr}^{-1}$) declined (Lynch et al. 1995; NADP 2002). A decline in SO_4^{2-} inputs can reduce soil solution SO_4^{2-} and base cation (C_B) concentrations and ultimately stream water fluxes (Driscoll et al. 1988, 2001; Likens et al. 2002). Change in SO_4^{2-} and NO_3^- deposition might also alter soil pH which in turn can affect soil microbial populations and nitrogen (N) mineralization rates (Binkley and Richter 1987; Hyman et al. 1998; Palmer et al. 2004).

We have studied the small (176-ha) Calumet watershed since 1979 (Stottlemeyer and Toczydlowski 1991, 1996a, b, 1999). The site is located along the south shore of Lake Superior (Figure 1). The few longer-term small watershed studies in the Upper Great Lakes region show strong retention of atmospheric DIN inputs (Turkey Lakes, Ontario: Foster et al. 1989; Calumet: Stottlemeyer and Toczydlowski 1991, 1996a, b; Wallace Lake: Stottlemeyer et al. 1998). For most of the 1980's, the Calumet watershed retained about 90% of atmospheric DIN inputs. However, during the last decade there has been an increase in watershed winter DIN output up to about one-third of inputs in some years. Almost all the increase was as NO_3^- -N.

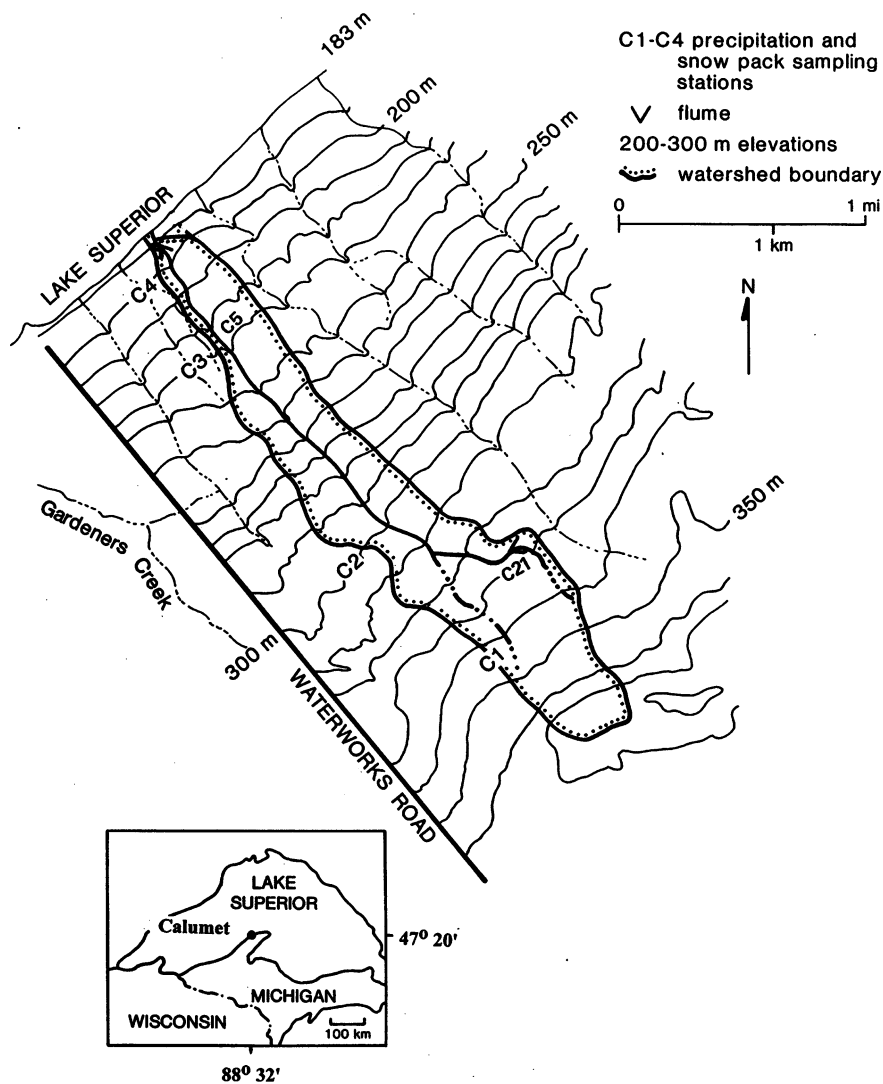


Figure 1. Location of Calumet watershed, Lake Superior Basin, Michigan.

Earlier we examined shorter-term data sets from this watershed to describe in detail change in hydrologic flowpath during winter, and to examine how sensitive stream water solute concentrations and flux might be to such changes (Stottlemeyer and Toczydowski 1991, 1999). Here we examine winter weather effects on seasonal flowpath and solute flux using data collected during the winters of 1987–2002. The study focus was on terrestrial flux of atmospheric inputs of H^+ , NO_3^- , NH_4^+ , and SO_4^{2-} , and forest floor DOC and DON. Our objectives were to (1) quantify the effect of change in winter temperature and

precipitation on snowpack peak water equivalent (PWE), watershed snowmelt volume, and soils on watershed solute flux, and (2) examine what ecosystem processes might account for differing time trends in solute outputs.

Methods

Site description

The 176-ha, first-order Calumet watershed is vegetated by 65–85-yr old sugar maple (*Acer saccharum* Marshall) and white birch (*Betula papyrifera* Marshall). The watershed is adjacent the south shore of Lake Superior, has a northwest aspect, uniform slope (average 5%), and moderate topographic relief (Figure 1). Watershed elevation varies from 190 m at the mouth to 370 m. The bedrock is predominantly Cambrian Freda sandstones overlain with alkaline till and old beach deposits. Soils are mainly Typic Haplorthods, sandy, mixed, frigid. Dominant horizons are O (7–0 cm), A (0–5 cm), E (5–13 cm), Bhs and Bsl (13–62 cm), BC (62–98 cm), and C (98 to > 200 cm). A nearly impervious soil layer (ortstein) occurs at 1.5–2 m depth. The weathering of alkaline till results in moderately buffered stream water at Calumet ($\text{ANC} = 595 \mu\text{eq l}^{-1}$) (Stottlemeyer and Toczydlowski 1991) and in much of the region (Wiener and Eilers 1987). The dominant stream water ions are Ca^{2+} and HCO_3^- , and in precipitation H^+ , NO_3^- , and SO_4^{2-} .

The climate along Lake Superior's south shore is modified by the lake which rarely freezes over. The open water moderates autumn and winter temperature extremes, and accounts for the region's high ($> 500 \text{ cm yr}^{-1}$) snowfall. Such conditions, coupled with daily maximum winter air temperatures approaching 0°C and unfrozen soils, result in periodic mid-winter thaws and small but steady snowmelt throughout much of winter.

Near Lake Superior snowfall amounts increase with small elevation gains (Stottlemeyer and Toczydlowski 1991, 1999). Spring snowmelt dominates the annual stream hydrograph. The first two-thirds of the rising limb of the spring hydrograph is dominated by snowmelt from the lower portion of the watershed (Toczydlowski and Stottlemeyer, unpub. data). Through peak discharge and most of the declining hydrograph limb watershed discharge is dominated by snowmelt from the upper watershed. Additional site details may be found in Stottlemeyer and Toczydlowski (1991, 1996a, b, 1999).

Field procedures

In 1979, four monitoring stations were located at intervals of increasing elevation in the watershed: C4 (190 m) near the mean elevation of Lake Superior, C3 (240 m), C2 (295 m) and C1 (350 m) (Figure 1). In winter, each station was equipped with a bulk collector (36 cm diameter) to measure both precipitation

quality and quantity. A transect (five sampling points) was established at each station where snowpack water equivalent (SWE) and depth were determined weekly using a Federal sampler that measured the moisture content of a snow core. The precipitation/snowpack stations were located in openings to minimize canopy debris in the collectors. Snowpack samples for chemical analyses were collected in a 10-cm-diameter PVC tube. In earlier study we measured throughfall in the watershed during two winters, but found no significant alteration of precipitation chemistry by the forest canopy.

For previous studies (Stottleyer and Toczydlowski 1996a, b, 1999), in autumn 1987 a fifth SWE transect and sampling station (C5) was established in the watershed between stations C3 and C4 about 35 m from the stream and upslope from the narrow riparian zone. Replicated plots were set up to conduct detailed study of snowpack, snowmelt, and soil water chemistry. Data from such plots can not be extrapolated to explain watershed-level processes. However, some of the 1988–2002 plot data are applicable to the objectives of the present study, and are included to complement watershed-level analyses. The field installation was as follows. Replicate (3) snow and soil lysimeter plots were installed. Each snowpack lysimeter consisted of a 2 × 3 m external cedar frame 15 cm in height and 2 cm thick. Each autumn a 0.15 mm polyethylene sheet was placed directly on the forest floor following leaf fall and attached to the frame. Melt water was directed by PVC tubing to a central 1.5 m deep pit with insulated cover. Within the pit, tipping bucket raingages recorded snowmelt volume from each snow lysimeter. Pit temperature and snowmelt rates were recorded by datalogger (Li-Cor, Lincoln, Nebraska).

Forest floor leachate was sampled using triplicate zero-tension lysimeter plots each in proximity to one of the snow lysimeters. Each plot consisted of three lysimeters made of PVC tubing cut in half (area 310 cm²) inserted beneath the forest litter layer. Each lysimeter was connected by 1.5 cm diameter PVC tubing to polyethylene bottles in small covered pits. Mineral soil solution was sampled from replicate (3) soil tension lysimeter plots each located in close proximity to one of the snow lysimeters. Each plot consisted of 3 lysimeters (ceramic cups, PVC tube, Soil Moisture Corp., Santa Barbara, California) at both 15 (A & E) and 30 cm (Bhs) soil depths.

Additional instrumentation at station C5 included dataloggers to record mean daily snowpack temperature at 10 and 40 cm above the forest floor, soil temperature at 5 cm depth beneath the Oi, daily mean and maximum/minimum air temperature; and solar radiation. Soil water wells were located at stations C5 and C21 away from the riparian zone, and each equipped with Stevens gauges (Leupold & Stevens, Beaverton, Oregon) to monitor change in soil water level above the impervious ortstein layer (<200 cm depth) during winter. We considered subsurface flow to be 'shallow' when it occurred within the top 25 cm of forest floor and soil organic layers [O (7–0 cm), A (0–5 cm), E (5–13 cm)].

Watershed discharge at the mouth was continuously monitored using a 30 cm wide Parshall flume equipped with Li-Cor datalogger and Stevens

pressure transducer. An additional instrument and stream sampling station was located at station C21 in the upper watershed at an elevation of approximately 320 m or between the elevations of stations C2 and C1. Its role was to monitor the relationship between snowpack melt, soil water level and stream discharge near the head of the watershed. Instrumentation was similar to that at the watershed mouth.

In the lysimeter plots, grab samples for chemical analyses were collected in linear polyethylene amber bottles from each snow lysimeter during the middle (4–5 p.m.) of the daily melt period. When meltwater release rates became more variable sampling frequency was increased. Beginning in late January, soil lysimeters were sampled about every 10 days until peak snowmelt at which time they were sampled more frequently. The zero tension lysimeters were sampled on a schedule similar to the soil solution lysimeters.

Watershed precipitation, snowpack and stream samples were collected weekly. During snowmelt, stream samples were collected more frequently based on a schedule developed from frequent sampling in earlier years (Stottleyer and Toczydlowski 1991). In some years there was significant diurnal change in discharge. During such times we sampled the stream daily at both the low and high discharge rates.

Stream water samples were collected just above the gauges using amber polyethylene 500 ml bottles. Additional subsamples were collected for the analyses of dissolved organic carbon (DOC) and in later years (1996–2002) dissolved organic nitrogen (DON). Only the samples retained for DOC/DON analyses were frozen.

Laboratory analyses

Samples were immediately brought into the laboratory at Michigan Technological University for initial processing and analyses. Snow samples were melted at room temperature in pre-rinsed, covered polyethylene containers. PH, electrical specific conductance, and alkalinity (titration with 0.02 N H₂SO₄ to pH 4.5) were determined as soon as samples reached room temperature. Filtered (pre-rinsed 0.45- μ m) subsamples were refrigerated (<3 °C) and chemical analyses for Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺, Cl⁻, NO₃⁻, PO₄⁻, and SO₄²⁻ were conducted using ion chromatography (Dionex Model 2020 IC, Sunnyvale, California). After 1991, samples were sent to our Bioanalysis Laboratory in Ft. Collins and ions analyzed on Waters ICs (Waters Corp., Milford, Massachusetts) equipped with Dionix columns.

Dissolved organic carbon (DOC) was determined in the early years on a Dohrmann 180 (Teledyne-Tekmar-Dohrmann, Mason, Ohio) carbon analyzer using filtered samples frozen in glass bottles. Since 1997, we have used a Shimadzu TOC-5000A analyzer (Shimadzu Scientific Instruments, Columbia, Maryland). Total dissolved nitrogen (TDN) was analyzed using an Antek 9000VN pyrochemiluminescent analyzer (Antek Instruments, L.P., Houston,

Texas) with CTC Leap autosampler (Justice Laboratory Software, Denville, New Jersey). The DON fraction was determined by subtracting DIN from TDN.

Laboratory quality assurance procedures included splitting weekly NADP samples (Michigan Station MI99), participation in the EPA's National Acid Precipitation Assessment Program (NAPAP) quality assurance (QA) checks up to 1990, continuous participation in the U.S. Geological Survey laboratory round robin program, routine use of NTIS and equivalent inorganic standards, and weekly comparisons of paired low-concentration cation results from atomic absorption (AA) and IC. Additional laboratory details are available at <http://www.fs.fed.us/rm/waterlab>.

Data analyses

The solutes examined in detail were selected to represent various source areas and processes within the watershed. Data analyses focused on estimating fluxes for atmospheric/snowmelt inputs of H^+ , NH_4^+ , NO_3^- , and SO_4^{2-} , and the dominant solutes in soil and stream water, Ca^{2+} , HCO_3^- , and DOC. Ca^{2+} was generally selected to represent the base cations (C_B) although all cations were included for descriptive purposes in some tables. NH_4^+ -N and NO_3^- -N were generally combined as dissolved inorganic nitrogen (DIN). However, stream water NH_4^+ concentrations were rarely above detection levels except during mid-winter thaws. Dissolved organic nitrogen (DON) was not consistently monitored until 1996, so it is not included in time trend estimates.

The present study focused on the winter period defined as December–April. April is the month of peak stream water discharge. Longer-term descriptive data on climate from the National Oceanographic and Atmospheric Administration (NOAA) were included for context. Time trend analyses for watershed data were confined to the period 1988–2002. We began analyzing well water chemistry in 1996 along with DON for many stations, and descriptive summaries without time trends for 1996–2002 are included. We emphasized solute flux at the watershed level for 1988–2002. Results from the replicated lysimeter plots and well data were used only as an indication of the potential importance of subsurface hydrology and the forest floor and surface mineral soils to modify snowmelt solute concentration and flux prior to reaching the stream. The plot setup and location were not designed or intended to be scaled up to the watershed level (see Stottlemyer and Toczydlowski 1996a). For solutes not included here, the concentrations for all macro ions and DOC have been included in previous cited Calumet studies.

For the limited comparisons between well water heights and stream water chemistry, we used only those years (1988, 1989, 1993, 1994, 1996, 1997, 2001) where a reasonable number (> 25) of stream samples could be collected when well water heights were approximately within 75 cm from the surface. Many years the rise in well water height was rapid limiting the opportunity for

concurrent soil lysimeter and stream water sampling (see Stottlemeyer and Toczydlowski 1999).

Solute input/output budgets were computed as follows. For precipitation, there was no correlation between precipitation amount and concentration. During most of the 1980 decade, we sampled precipitation chemistry and amount at four stations (C1–C4, Figure 1) along the elevation gradient. While precipitation amount significantly increased with elevation, solute concentration did not change. Thus we estimated solute inputs using the chemistry at station C4 and the average precipitation amount among all stations. Atmospheric inputs were calculated using the mean weekly concentrations times the total amount of precipitation that fell. For solute output in stream flow, during winter prior to snowmelt weekly output was estimated using the concentration of the weekly sample times the discharge for equal time periods before and after the sample date. During the snowmelt period, stream water was sampled more frequently dependent upon the variation in the hydrograph. Sampling was done daily or more frequently to quantify concentration at timed intervals along the daily hydrograph. Outputs were estimated from the mean concentration times the total discharge for the week. Weekly values were then summed by month, quarter, and for the entire winter study period.

The snowpack water equivalent (SWE) and its solute content were estimated as follows. During a pre-study period (1979–1982), we periodically measured the SWE along contour lines at elevations similar to stations C1–C4. The SWE and its solute content increased significantly with elevation but did not vary significantly within a given contour. This finding might be expected in a long, relatively narrow watershed with little shift in aspect east or west (Figure 1). For the present study, watershed SWE and solute content were estimated by taking the mean SWE for three locations at each station times the solute concentration; then computing the mean among the four stations C1–C4.

For the replicated snowpack, snowmelt, forest floor and soil solution plots at station C5, snowpack sublimation and evaporation were estimated by the differences between weekly precipitation and SWE when there was little or no snowmelt, and by the differences between precipitation, SWE, and snowmelt (cm) during the snowmelt period. Snowmelt did not occur every day even late in winter because of periodic cold periods. So snowmelt solute flux was estimated by taking the daily concentration times the snowmelt volume and summing for week, month, or entire winter. As mentioned earlier, we did not extrapolate plot results to the watershed level.

The study was relatively short-term (1988–2002). For analyses related to time trends in solute flux, Lowess plots, a smoothing method that finds a predicted value of Y for each X from a weighted average of nearby Y values, were used to visually examine data prior to fitting a model. A tension of 0.5 was used. If the Lowess analysis indicated a curvilinear trend, data transformations were made to see if a fit better than a linear model might exist. If the Lowess analysis showed a reversal in slope, the significances of slopes were examined. Systat Multivariate General Linear Hypothesis (MGLH) subroutines were

used which present standard error of the estimate, and analysis of variance (Anova) tables to estimate model fit. The hydrology of small snow-dominated watersheds is highly variable. The homogeneity of variance in the residuals was checked visually by plotting residuals against estimates.

The regressions on time series data were checked for autocorrelation by examining the independence of residuals using the Durbin–Watson D and autocorrelation statistics. For second-order and lower autocorrelation, the Systat Series subroutine was used to check for correlation with lag (Wilkinson et al. 1996).

Results

Temperature and hydrology

Mean annual air temperatures increased ($p < 0.001$, $r^2 = 0.18$, $b = 0.03 \text{ }^\circ\text{C yr}^{-1}$) during 1950–2002 at NOAA station 3908, 8 km south of the Calumet watershed. Most of the temperature gain was in winter. Since 1988, when the present study began, winter temperatures averaged $0.7 \text{ }^\circ\text{C}$ warmer than the previous 30 years. All winter months showed an increase in temperature and summer months a decline. Most of the temperature increase occurred in November and February but the trends with time were not significant (Figure 2). In the Calumet watershed, during the week prior to snowpack formation the mean daily soil temperatures at station C5 increased ($p < 0.01$, $r^2 = 0.53$, $b = 0.1 \text{ }^\circ\text{C yr}^{-1}$, Figure 3). Soil temperatures beneath the snowpack throughout winter also increased but not significantly.

Annual precipitation at NOAA station 3908 declined since 1950, but the relationship with time was weak ($p < 0.05$, $r^2 = 0.07$, $b = -0.3 \text{ cm yr}^{-1}$). Since 1988, when the present study began, the decline in NOAA precipitation was $> 2 \text{ cm yr}^{-1}$ ($p < 0.01$, $r^2 = 0.45$, Figure 2). Most of the annual decrease occurred in winter especially the months of November ($p < 0.05$, $r^2 = 0.25$, $b = -0.3 \text{ cm yr}^{-1}$) and February ($p < 0.01$, $r^2 = 0.46$, $b = -0.6 \text{ cm yr}^{-1}$). In the Calumet watershed, winter precipitation (December–April) also declined about 1 cm yr^{-1} ($p < 0.001$, $r^2 = 0.54$).

The time a snowpack was present decreased during the study, the snowpack was lost earlier, and peak stream water discharge with snowmelt declined. However, no time trend was significant. At the replicated plots near C5 there was no time trend in snowpack sublimation plus evaporation, peak water equivalent (PWE) or correlation between PWE and total snowmelt. Snowmelt and seasonal precipitation were correlated ($p < 0.05$), and the snowmelt amount declined during the study ($p < 0.05$, $r^2 = 0.29$, $b = -0.8 \text{ cm yr}^{-1}$, standard error (SE) of constant = 29.9, of slope = 0.31, Figure 4). In the week preceding peak stream water discharge, 41% (range 13–93%) of total snowmelt occurred. The percentage increased during the study, but not significantly.

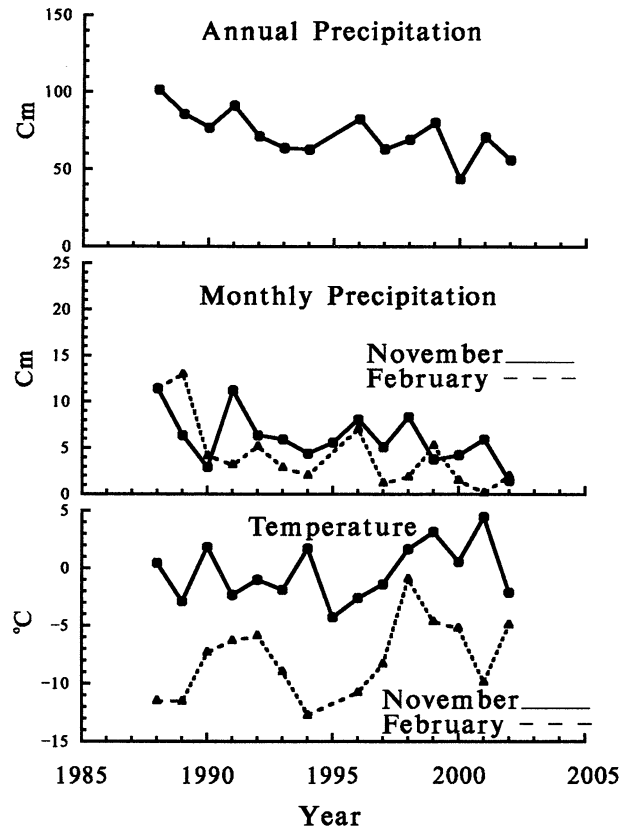


Figure 2. Annual precipitation, monthly precipitation and temperature for November and February, 1988–2002, NOAA station 3908, Houghton–Hancock County Airport, Michigan.

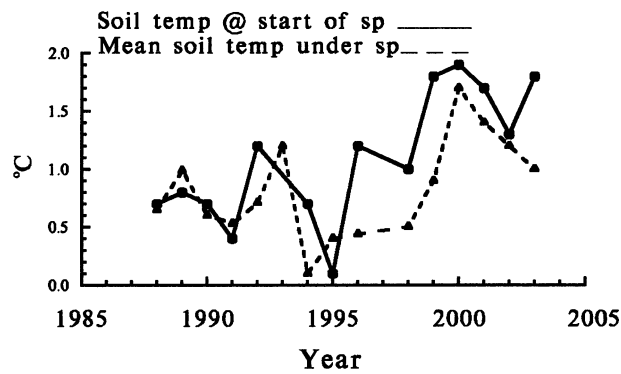


Figure 3. Soil temperatures (5 cm beneath Oi) for week before snowpack formed, and at 5 cm beneath the Oi and snowpack throughout winter, 1988–2003, station C5, Calumet watershed, Michigan. Data shown for 2003 not included in analyses.

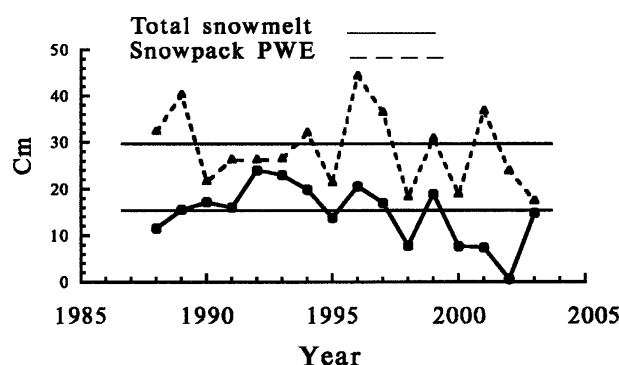


Figure 4. Total snowmelt and snowpack PWE, 1988–2003, Calumet watershed, Michigan. Horizontal lines show mean snowmelt and PWE for period of study. Data shown for 2003 not included in analyses.

Annual watershed runoff declined ($p < 0.001$, $r^2 = 0.48$, $b = -1.04 \text{ cm yr}^{-1}$, SE constant = 23.78, SE $b = 0.26$) during the study. Annual runoff and precipitation were not correlated. Annual runoff was dominated ($p < 0.001$) by snowmelt, but annual runoff and snowmelt were not correlated. There was no correlation between annual runoff and peak daily snowmelt, snowmelt timing, or snowpack PWE.

Winter runoff also declined during the study, but the time trend was not significant (Figure 5). Winter runoff was related to winter precipitation amount ($p < 0.05$, $r^2 = 0.26$). The percentage of total winter runoff that occurred when the plot-level subsurface lateral flow was shallow (<25 cm depth beneath forest floor Oi layer) increased during the study ($p = 0.05$, $r^2 = 0.25$, $b = 2\% \text{ yr}^{-1}$, SE of constant = 46.7, SE of $b = 0.5$). Stream water snowmelt discharge increased on average 5.6 ± 2.4 days prior to a rise in plot-level well water levels (also see Stottlemyer and Toczydowski 1999).

Atmospheric inputs and snowpack solute content

Annual inputs at NADP station MI99, 16 km south of the Calumet watershed, showed few time trends except for declines in H^+ ($p < 0.01$, $r^2 = 0.32$, $b = -0.004 \text{ kg ha}^{-1} \text{ yr}^{-1}$), SO_4^{2-} ($p < 0.05$, $r^2 = 0.27$, $b = -0.25 \text{ kg ha}^{-1} \text{ yr}^{-1}$), and Cl^- ($p < 0.05$, $r^2 = 0.26$, $b = -0.02 \text{ kg ha}^{-1} \text{ yr}^{-1}$). At Calumet winter solute inputs declined for H^+ ($p < 0.01$, $r^2 = 0.59$, $b = -0.003 \text{ kg ha}^{-1} \text{ yr}^{-1}$), NO_3^- ($p < 0.05$, $r^2 = 0.36$, $b = -0.03 \text{ kg ha}^{-1} \text{ yr}^{-1}$), NH_4^+ ($p < 0.01$, $r^2 = 0.45$, $b = -0.02 \text{ kg ha}^{-1} \text{ yr}^{-1}$), DIN ($p < 0.01$, $r^2 = 0.45$, $b = -0.05 \text{ kg ha}^{-1} \text{ yr}^{-1}$), and SO_4^{2-} ($p < 0.001$, $r^2 = 0.69$, $b =$

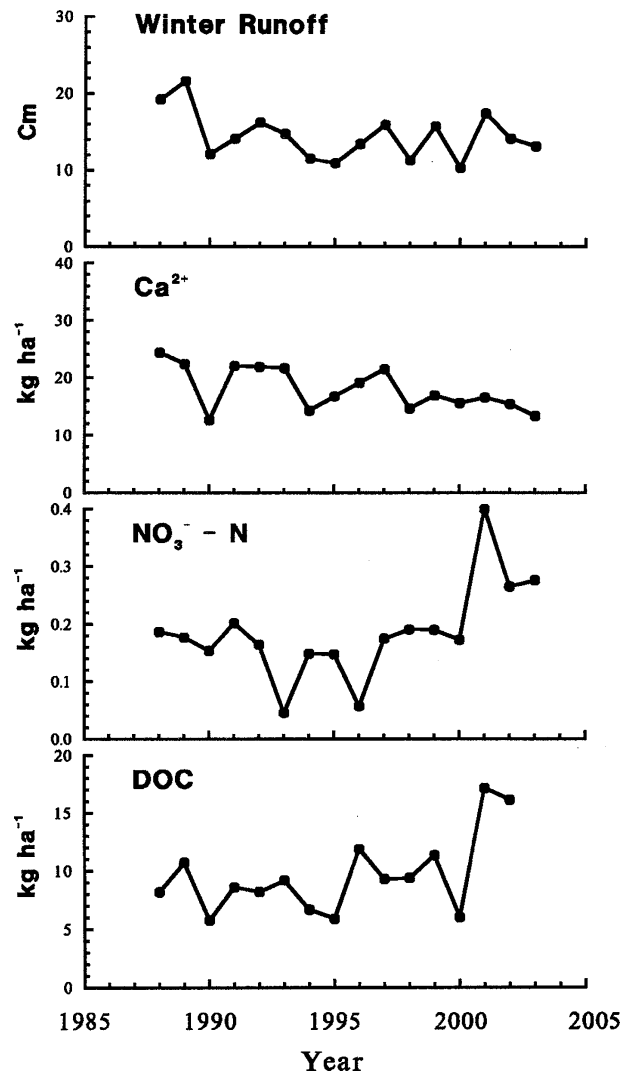


Figure 5. Winter runoff and outputs for selected solutes, 1988–2003, Calumet watershed, Michigan. Data for 2003 not included in analyses.

$-0.15 \text{ kg ha}^{-1} \text{ yr}^{-1}$) (Figure 6). During the study, winter precipitation amount declined 48%, the input of H^+ declined 55%, NH_4^+ 60%, NO_3^- 52%, DIN 50%, and SO_4^{2-} 70%.

The Calumet snowpack PWE and its solute content generally decreased during the study, but only the declines in H^+ , NO_3^- , SO_4^{2-} , and Cl^- were significant (Table 1). The peak snowpack H^+ , NO_3^- , and SO_4^{2-} contents were correlated ($p < 0.01$).

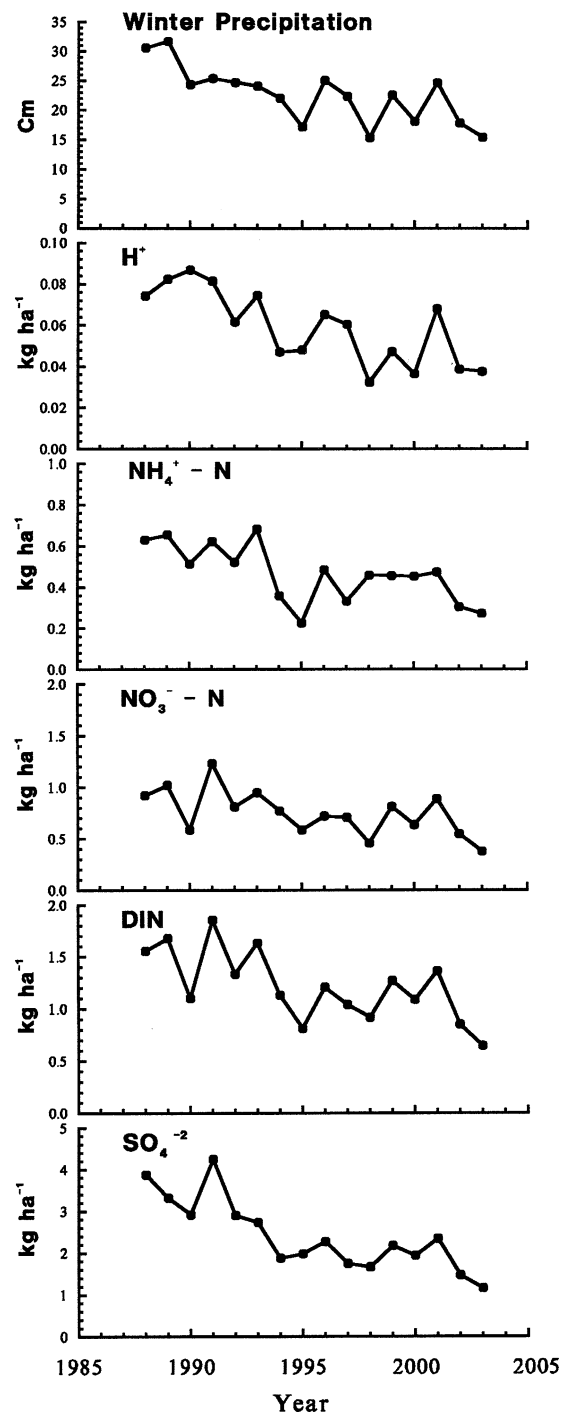


Figure 6. Time trend for winter (December–April) precipitation amount and solute inputs, 1988–2002, Calumet watershed, Michigan (only significant trends shown).

Forest floor, soil water, stream water solute concentrations

The replicated plot lysimeter and well water chemistry essentially represented a mid-elevation point in the watershed while the stream water chemistry the entire watershed. Still there were some relationships between the two that supported other study findings (Tables 2 and 3).

Table 1. Time trends for snowpack peak water equivalent (PWE) and content of selected solutes, 1988–2002, Calumet watershed, Michigan.

	<i>p</i>	<i>r</i> ²	<i>b</i> (kg ha ⁻¹ yr ⁻¹)	SE ^a constant	SE <i>b</i>
PWE	ns				
Ca ²⁺	ns				
K ⁺	ns				
NH ₄ ⁺	ns				
H ⁺	0.01	0.26	-0.0003	0.11	0.0001
NO ₃ ⁻ -N	0.05	0.20	-0.12	4.55	0.05
DIN ^b	ns				
SO ₄ ²⁻	<0.001	0.39	-0.17	4.09	0.04
Cl ⁻	<0.05	0.30	-0.21	7.14	0.08

(ns = not significant).

^aSE = standard error.

^bDIN = dissolved inorganic nitrogen or sum of NO₃⁻-N and NH₄⁺-N.

Table 2. Time trends in soil lysimeter solute concentrations, 1988–2002, Calumet watershed, Michigan.

Solute	<i>p</i>	<i>r</i> ²	<i>b</i> (mg l ⁻¹ yr ⁻¹)	SE ^a constant	SE <i>b</i>
Forest floor lysimeters					
Na ⁺	0.05	0.32	-0.02	0.67	0.007
NH ₄ ⁺	<0.01	0.47	-0.02	0.49	0.005
SO ₄ ²⁻	<0.05	0.31	-0.13	5.07	0.05
Cl ⁻	<0.05	0.32	-0.04	1.38	0.01
Lysimeters at 15 cm depth					
Ca ²⁺	<0.001	0.88	-0.16	1.52	0.01
Mg ²⁺	<0.001	0.78	-0.03	0.35	0.004
SO ₄ ²⁻	<0.01	0.49	-0.16	4.28	0.04
Cond	<0.01	0.39	-0.62 μmhos l ⁻¹	19.9	0.2
Lysimeters at 30 cm depth					
Ca ²⁺	<0.01	0.54	-0.11	2.72	0.03
Mg ²⁺	0.01	0.40	-0.01	0.73	0.01
NH ₄ ⁺	<0.05	0.28	-0.01	0.25	0.003
SO ₄ ²⁻	<0.05	0.30	-0.08	3.17	0.03
DOC	<0.05	0.33	0.3	13.55	0.14

Only soil water solutes with a significant trend are shown.

^aSE = standard error of estimates.

Table 3. Correlation coefficients between weekly mean well water and stream water concentrations for selected solutes, 1997–2002, Calumet watershed, Michigan.

	Ca ²⁺ (S)	Ca ²⁺ (W)	NO ₃ ⁻ (S)	NO ₃ ⁻ (W)	SO ₄ ²⁻ (S)	SO ₄ ²⁻ (W)	DOC (S)	DOC (W)
Ca ²⁺ (S)	1.00							
Ca ²⁺ (W)	0.40*	1.00						
NO ₃ ⁻ (S)	-0.05	-0.60***	1.00					
NO ₃ ⁻ (W)	0.22	-0.51*	0.69***	1.00				
SO ₄ ²⁻ (S)	0.07	-0.60***	0.76***	0.51**	1.00			
SO ₄ ²⁻ (W)	0.36*	0.32	-0.40*	-0.71**	-0.24	1.00		
DOC (S)	0.09	-0.52*	-0.15	0.31	-0.133	-0.21	1.00	
DOC (W)	0.22	-0.36	-0.68**	0.07	-0.29	-0.33	0.84***	1.00

Routine well water chemical analyses started late in 1996. H⁺ data are not included since lowest pH in well water was only 5.93 (1.1 μeq H⁺ l⁻¹) and in stream 7.25 (0.05 μeq H⁺ l⁻¹). S = stream water, W = well water.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

Forest floor leachate Na⁺, NH₄⁺, SO₄²⁻, and Cl⁻ concentrations declined during the study (Table 2). For soil lysimeters at the 15 cm depth, Ca²⁺, Mg²⁺, and SO₄²⁻ concentrations decreased with time. The three solute concentrations were correlated ($p < 0.01$). The decline in SO₄²⁻ could account for 31% of the decrease in Ca²⁺ and Mg²⁺ (equivalent charge). At 30 cm soil depths, Ca²⁺, Mg²⁺, NH₄⁺, and SO₄²⁻ declined while the DOC concentration increased. The decline in SO₄²⁻ concentration could account for about 25% of the decrease in Ca²⁺ and Mg²⁺. For solutes with a concentration time trend at multiple depths, SO₄²⁻ showed the greatest decrease in forest floor leachate and soil solution at 15 cm. In soil solution, the decline in Ca²⁺ and Mg²⁺ concentrations was greatest at the 15 cm depth.

Watershed DON concentration was only systematically monitored since 1996 so time trend analyses were not possible. The DON concentrations were greater than DIN in lysimeter soil solution at 15 (DON/DIN = 4, $p < 0.001$) and 30 cm (DON/DIN = 4.2, $p < 0.001$) depths. The DON and DIN concentrations did not differ in forest floor leachate, well water, or stream water.

Increased well water heights were related to declines in stream water Ca²⁺ ($p < 0.001$, $r^2 = 0.87$, $b = -0.07$ mg l⁻¹ cm⁻¹), HCO₃⁻, ($p < 0.001$, $r^2 = 0.82$, $b = -0.23$ mg l⁻¹ cm⁻¹), and Cl⁻ ($p < 0.001$, $r^2 = 0.62$, $b = -0.005$ mg l⁻¹ cm⁻¹) concentrations and to a lesser extent SO₄²⁻ ($p < 0.01$, $r^2 = 0.10$, $b = -0.09$ mg l⁻¹ cm⁻¹). There was a positive relationship between increased well water heights, stream discharge, and stream water DOC concentration ($p < 0.001$, $r^2 = 0.23$, $b = 0.03$ mg l⁻¹ cm⁻¹).

Stream water Ca²⁺ concentrations were correlated with well water Ca²⁺ and SO₄²⁻ while well water Ca²⁺ concentrations were inverse with stream water NO₃⁻, SO₄²⁻, DOC, and well water NO₃⁻ concentrations (Table 3). Stream water NO₃⁻ concentrations were correlated with well water NO₃⁻ and stream water SO₄²⁻, and

Table 4. Relationship between winter stream discharge and solute concentration, 1988–2002, Calumet watershed, Michigan.

Solute	<i>p</i>	<i>r</i> ²	<i>b</i> mg l ⁻¹	SE ^a constant	SE <i>b</i>
Ca ²⁺	< 0.001	0.41	-0.05	0.24	0.004
Mg ²⁺	< 0.001	0.35	-0.01	0.03	0.001
Na ⁺	< 0.001	0.30	-0.005	0.03	0.001
K ⁺	ns				
H ⁺	ns				
NH ₄ ⁺	ns				
NO ₃ ⁻	ns				
SO ₄ ²⁻	ns				
Cl ⁻	< 0.001	0.33	-0.003	0.02	< 0.001
HCO ₃ ⁻	< 0.001	0.55	-0.12	0.49	0.009
cond	< 0.001	0.57	-0.26 μmhos l ⁻¹	0.97	0.018
DOC	< 0.001	0.32	0.02	0.21	0.003

^aSE = standard error of constant and slope (*b*).

were inverse with well water SO₄²⁻ and DOC concentrations. Well water NO₃⁻ concentrations were inverse to SO₄²⁻ but correlated with stream water SO₄²⁻. Stream and well water DOC concentrations were correlated.

Most stream water base cation (*C*_B), Cl⁻, and HCO₃⁻ concentrations declined with increased stream water discharge, K⁺, NO₃⁻, and SO₄²⁻ were unchanged, and DOC increased (Table 4). Since 1996, during which we sampled both DOC and DON concentrations and flux throughout the snowmelt hydrograph, DIN (*p* < 0.01, *r*² = 0.30, *b* = 0.001 mg l⁻¹), DON (*p* < 0.001, *r*² = 0.60, *b* = 0.002 mg l⁻¹), and DOC (*p* < 0.001, *r*² = 0.63, *b* = 0.04 mg l⁻¹) concentrations increased with discharge while the DOC/DON ratio declined (*p* < 0.01, *r*² = 0.32, *b* = -0.2).

During the 1988–2002 study, winter volume-weighted stream concentrations of H⁺ declined (*p* = 0.01, *r*² = 0.39) while *C*_B, NH₄⁺, SO₄²⁻, Cl⁻, and HCO₃⁻ concentrations showed no trends. In contrast, winter volume-weighted stream water concentrations of NO₃⁻-N (*p* < 0.05, *r*² = 0.30) and DOC (*p* = 0.01,

Table 5. Average winter fluxes for selected solutes, Calumet watershed, 1988–2002.

Component	Amount (cm)	H ⁺ (kg ha ⁻¹)	NO ₃ ⁻ -N (kg ha ⁻¹)	NH ₄ ⁺ -N (kg ha ⁻¹)	SO ₄ ²⁻ (kg ha ⁻¹)	DOC (kg ha ⁻¹)
Precipitation ^a	31.0	0.020	1.23	1.34	5.31	0.70
Snowpack PWE ^a	29.0	0.006	0.94	0.51	3.28	0.96
Forest floor ^b	16.0	0.010	0.40	0.12	3.03	53.90
15 cm depth ^b	16.0	0.003	0.11	0.02	6.45	22.60
30 cm depth ^b	16.0	< 0.001	0.20	0.02	5.51	13.30
Stream output ^a	18.5	< 0.001	0.16	0.05	8.36	9.10

^aAt watershed level.

^bMid-elevation, replicated snow and soil lysimeter plots.

$r^2 = 0.39$) increased. Peak stream water DOC concentrations during spring runoff also increased ($p < 0.01$, $r^2 = 0.40$, $b = 0.31 \text{ mg l}^{-1} \text{ yr}^{-1}$).

Forest floor, soil, stream water solute flux

The forest floor and surface mineral soils in the plots modified precipitation and snowmelt solute flux (Table 5). Eighty percent of precipitation N input was retained as meltwaters passed through the forest floor, and 95% by the 15+ cm soil depth. There was little subsequent change in inorganic N flux at the plot level. Conversely, SO_4^{2-} flux at the 30 cm depth was nearly equal precipitation inputs, and DOC flux was 15 times snowmelt input. The watershed retained >95% of winter NH_4^+ -N inputs, 87% of NO_3^- -N inputs, and >99% of H^+ inputs. Stream SO_4^{2-} output exceeded input by 60%, and DOC output was an order-of-magnitude greater than input.

Winter stream water solute export significantly increased with discharge ($p < 0.001$, $r^2 = 0.23\text{--}0.90$). The increase in flux cm^{-1} discharge averaged 180% of mean winter flux with the increases greatest for K^+ ($p < 0.001$, $r^2 = 0.37$, $b = 0.68 \text{ kg ha}^{-1} \text{ cm}^{-1}$), DIN ($p < 0.001$, $r^2 = 0.76$, $b = 0.03 \text{ kg ha}^{-1} \text{ cm}^{-1}$), and SO_4^{2-} ($p < 0.001$, $r^2 = 0.92$, $b = 0.53 \text{ kg ha}^{-1} \text{ cm}^{-1}$).

Winter stream water Ca^{2+} , Mg^{2+} , and HCO_3^- outputs declined with time while the remaining C_B , SO_4^{2-} , and Cl^- were unchanged (Table 6, Figure 5). Outputs of Ca^{2+} , Mg^{2+} , SO_4^{2-} , and HCO_3^- were correlated ($p = 0.01$). Winter outputs were not correlated with the time that subsurface flow was shallow (< 25 cm depth beneath the Oi) or the percentage of total winter runoff and stream discharge that occurred during that period.

Table 6. Time trends in annual (period of record) and winter stream water discharge (cm) and solute flux (kg ha^{-1}), 1988–2002, Calumet watershed (ns = not significant).

	Annual (1980–2002)			Winter (1988–2003)		
	<i>p</i>	r^2	<i>b</i> (kg ha^{-1})	<i>p</i>	r^2	<i>b</i> (kg ha^{-1})
Discharge	<0.001	0.48	−1.01 ^a	ns		
Ca^{2+}	<0.001	0.49	−43.00	<0.05	0.37	−0.58
Mg^{2+}	<0.05	0.25	−0.11	<0.01	0.55	−0.09
Na^+	ns			ns		
K^+	ns			ns		
H^+	<0.01	0.39	−0.00002	ns		
NH_4^+ -N	ns			ns		
NO_3^- -N	0.05	0.19	0.03	0.05	0.29	0.01
SO_4^{2-}	ns			0.06		
Cl^-	ns			ns		
HCO_3^-	<0.01	0.36	−2.31	<0.05	0.46	−1.47
DOC	ns			0.06		

^aDischarge in cm.

Table 7. Correlation coefficients for total stream discharge and percentage of total winter discharge (DSCHG) when subsurface flow was shallow (<25 cm depth beneath Oi); and total winter Ca^{2+} , dissolved inorganic nitrogen (DIN), and DOC outputs, 1988–2003, Calumet watershed, Michigan.

	Discharge	% DSCHG	Ca^{2+}	DIN	DOC
Discharge	1.00				
% DSCHG	0.94***	1.00			
Ca^{2+}	0.04	-0.16	1.00		
DIN	0.58*	0.67**	-0.16	1.00	
DOC	0.83***	0.70**	-0.05	0.57*	1.00

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

In contrast, winter NO_3^- -N outputs increased during 1988–2002 (Figure 5). The peak weekly DOC output also increased with time ($p < 0.01$, $r^2 = 0.47$, $b = 0.24 \text{ kg ha}^{-1} \text{ yr}^{-1}$). Winter stream water DOC and DIN outputs were correlated (Table 7). Total winter DOC output was correlated with the elapsed time that subsurface flow was shallow, and the percentage of winter runoff and stream discharge that occurred during that time. Total winter DIN output was correlated with the percentage of winter runoff and stream discharge that occurred when subsurface flow was shallow.

Discussion

Temperature and hydrology

Throughout the region temperatures have been warming for at least several decades with most of the increase in winter. The NOAA station 3908 has the only long-term climate record in the vicinity of the Calumet watershed. The two warmest years in the 50+-year record for station 3908 occurred in 1987 and 1998. Throughout the region since 1987 annual temperatures have warmed about $0.1 \text{ }^\circ\text{C yr}^{-1}$ (NOAA 2002). Similar warming has also occurred at the Experimental Lakes Area in southwest Ontario (Schindler et al. 1997). At NOAA station 3908 almost all warming occurred in autumn and winter months especially November, December, and February. However, only the February trend was significant ($0.3 \text{ }^\circ\text{C yr}^{-1}$). Lowess plots of the NOAA data indicate little or no temperature trend in November and February temperatures up to 1995, then an increase of $> 1 \text{ }^\circ\text{C yr}^{-1}$ during 1995–2002.

The Lowess plot of Calumet soil temperatures the week prior to snowpack formation (Figure 3) also showed only a slight rate of gain during 1988–1995, then a rise in temperatures of about $0.2 \text{ }^\circ\text{C}$ each winter through 2002. A similar plot showed the mean soil temperature beneath the snowpack declined about $0.1 \text{ }^\circ\text{C}$ each winter during 1988–1995, then reversed slope increasing almost

0.2 °C each winter up through 2002. The warming winter temperatures and decline in snowpack presence did not result in sufficient loss of snowpack insulation to freeze soils at our monitoring stations in mid-winter. Soil freeze-thaw cycles can have a major effect on forest floor and soil nitrification rates and subsequent solute output, especially NO_3^- -N, during spring snowmelt (Mitchell et al. 1996; Fitzhugh et al. 2003).

The region also appears to be in a multi-decade period of declining precipitation with most of the decrease in winter. During this study, the decline in annual precipitation was similar in magnitude to that observed from 1970–1990 at the Experimental Lakes Area (Schindler et al. 1997). In 2000 and 2002, annual precipitation at NOAA station 3908 fell below the range of the previous 50+ years, the period of record. The decline in annual and winter precipitation at Calumet continued a trend seen throughout the 1980's (Stottlemyer and Toczydlowski 1996b). In the present study, Lowess plots of both the Calumet and NOAA data showed a little or no winter precipitation decline for 1993–1997, then a return to the rate of decline (2+ cm each winter) observed from 1987–1993 (Figure 6). Winter weekly precipitation amounts and solute inputs at Calumet also decline (Stottlemyer and Toczydlowski 1996a).

At Calumet, we attribute the lack of a significant time-trend in snowpack conditions to the warmer and drier winters that resulted in the high year-to-year variation in SWE and PWE (Figure 4), and the rather short study period (1988–2002). The Lowess plot results showed a slight increase in winter snowmelt amount up to 1994, then a decline of almost 2 cm each winter during 1995–2002. In winter 2002, November and February precipitation amounts were near or at record lows (Figure 2), temperatures near record highs, and soil temperature beneath the snowpack at station C5 near the record high. This combination of factors coupled with greater snowpack sublimation/evaporation resulted in a record low snowmelt (1 cm) at station C5 for the winter (Figure 4). The watershed-level snowpack PWE in 2002 was driven by amounts from the upper half of the watershed (PWE at station C2 = 13 cm, C1 = 24 cm). The lower than average snowpack PWE most years after 1997 (Figure 4) contributed to the reduced snowmelt. The Lowess plot showed little change in snowpack PWE for the period 1988–1997, then a decline of about 1.5 cm each winter. Such factors and their interaction help account for the high variation in hydrology and solute fluxes in small snow-dominated watersheds.

Our earlier studies further quantified the large variation in snowpack PWE and snowmelt timing and rates in the watershed (Stottlemyer and Toczydlowski 1996b). In the early 1980's, snowpack PWE varied >3-fold in 3 years. We have continuously monitored snowpack and soil temperatures throughout winter (D. Toczydlowski, Michigan Tech University, unpub. data), and periodic mid-winter thaws are the rule. Such conditions set the stage for wide variation in mid-winter and peak snowmelt amounts and rates, and account for the absence of correlation between snowpack PWE and total snowmelt. On average, the snowpack water equivalent (SWE) declines 25–35% prior to PWE (Stottlemyer and Toczydlowski 1996b). The SWE reduction results in the

snowpack losing, through differential solute elution, about 50% of its solute load prior to peak snowmelt. But even during rapid snowmelt, >90% of the snowmelt enters the forest floor and surface mineral soils (Stottlemyer and Toczydlowski 1991).

At the station C5 replicated plots, shallow subsurface lateral flow (well water levels <25 cm beneath Oi) during snowmelt occurred on average 12 days (range 2–17 days) each winter or <10% of the winter study period. However, during that time, which immediately followed the maximum snowmelt rate, 25–30% of the winter runoff occurred. During 1988–2002 there was a trend of increased number of days that shallow subsurface flow occurred, but it was not significant ($p = 0.07$). Residual analyses showed that low numbers of days in 1995 and 1997 were unusual, and when removed the time trend was significant ($p < 0.02$). In Figures 2–5 there is no obvious explanation for why 1995 and 1997 had short time periods of shallow subsurface flow. However, the stream snowmelt hydrographs (not shown) for both years were not characterized by the usual large single peak, but by peak discharge about 50% of average with multiple small peaks extending for a period of time.

Our earlier research showed a correlation ($p < 0.001$, $r^2 = 0.5–0.9$) between winter daily stream water discharge and change in soil water levels at the monitoring wells (Stottlemyer and Toczydlowski 1999). This correlation indicates the potential importance of shallow soil macropore flow in the winter hydrologic budget. If what was recorded at the replicated plots was present at the watershed level, the increase in time that shallow subsurface flow occurred during the present study could account for why winter runoff (Figure 5) did not decline the extent that winter precipitation did. The trend toward more snowmelt the week prior to peak stream water discharge likely contributed to the increase in shallow subsurface flow.

Lowess analyses of the winter time trend in Calumet runoff (Figure 5) showed a decline up to 1995 then a leveling off. Linear regression for that 1988–1995 period showed a decline ($p < 0.05$, $r^2 = 0.57$, $b = -1.7 \text{ cm yr}^{-1}$) with no significant change during 1995–2002.

Winter stream water discharge accounted for most of the variation in solute flux. About 56% of annual runoff occurs in winter (Stottlemyer and Toczydlowski 1996b). We attribute the lack of a relationship between annual runoff and precipitation to the reduced ratio of runoff to precipitation during the growing season and early autumn. Precipitation increases during summer and early autumn. But because of canopy interception and evaporation, and the increase in hardwood forest transpiration, the stream hydrograph rarely responds to even moderate summer rains.

Solute concentrations

The soil lysimeter results from the replicated mid-elevation plots can not be scaled up to the watershed level. However, the plot results provided some

indication of the potential for over-winter solute pools and soil processes in the forest floor and shallow mineral soils to modify precipitation and snowmelt inputs. From the plot results, it appeared the decline in SO_4^{2-} soil solution concentrations (Table 2) only accounted for about a third of the decline in Ca^{2+} and Mg^{2+} . The increased soil solution DOC concentration, on an equivalent basis ($8 \mu\text{eq mg}^{-1}$ DOC), accounted for much of the remainder. This finding was consistent with our earlier Calumet studies which showed DOC the dominant anion in shallow (15–30 cm depth) soil solution (Stottlemeyer and Toczydlowski 1996b).

The percentage of precipitation N retained in the forest floor (80%) and surface mineral soil (93%) of the mid-elevation plots was consistent with findings from control and N-amended plots in hardwood forests at Bear Brook, Maine, and the Harvard Forest (Aber et al. 1993; Magill et al. 1996). Our estimates of N retention in the plots suggest there was little subsequent in-stream N uptake. Winter in-stream processes that could alter limiting nutrient budgets are less important than in other seasons (Mulholland and Hill 1997).

During the 16-year study the increase in stream water DIN concentration, almost all of which was NO_3^- -N, could have been caused by reduced forest N retention as the successional forest aged. We have measured seasonal N mineralization rates in the watershed (Stottlemeyer and Toczydlowski 1996a), but not for a multi-year period. And we do not have estimates of N uptake by the hardwood forest for this time period. However, numerous studies in other successional hardwood forests suggest little change or a gain in N uptake for similar forest vegetation and age. At Hubbard Brook, the 55-year old mixed hardwood forest accumulated N both above- and below-ground (Likens and Bormann 1995). Both model (JABOWA) and long-term measurements generally show northern hardwood forests to continue accumulating biomass and nutrients up to almost 100 years of age (Bormann and Likens 1979). At Turkey Lakes, Ontario, just to the northeast of Lake Superior, soil solution NO_3^- concentrations are greater than at Calumet and are correlated with soil and stream water NO_3^- concentrations (Foster et al. 1989). However, Turkey Lakes is vegetated by much older northern hardwood forest, and soil and stream water NO_3^- still contributes little to C_B flux compared with HCO_3^- or SO_4^{2-} . At Calumet, further evidence that there was little change in terrestrial DIN availability during 1988–2002 comes from the absence of a time trend in DIN concentrations in forest floor leachate or soil solution (Table 2).

Some studies of similar duration have shown concurrent trends in soil and stream water solute concentrations (Palmer et al. 2004). The Calumet plot-level data indicate that change in soil solution solute concentrations could explain a portion of concentration change in stream water. Except for DOC, all soil water solute concentrations declined during the study period though the trend for most was not significant. This finding suggests that dilution was likely the dominant driver determining most shallow (0–30 cm depth) soil solute concentration trends. In addition, for the few solutes in soil water with time trends at multiple depths (Ca^{2+} , Mg^{2+} , SO_4^{2-}), the rate of decline was most evident in

the shallowest depths (Table 2). Since winter precipitation decreased during the study and snowpack PWE and stream runoff showed general, but not significant, declines, the greater dilution rate of solute concentrations in shallow soil solution was further evidence of an increase in snowmelt lateral flow at shallower soil depths. However, again caution must be used in any data extrapolated from three mid-elevation points (plots) to explain cause-effect at the watershed level.

The DON data collected only during 1996–2002 indicate no difference between winter stream water DON and DIN concentrations ($\text{DON}/\text{DIN} = 0.8$) and export from the watershed. Other investigators have hypothesized that stream water DIN concentration should exceed DON in regions of elevated atmospheric DIN inputs (Perakis and Hedin 2002; Vanderbilt et al. 2003). The annual DIN inputs at Calumet (average wet deposition $4.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) are 15 times greater than found at higher latitudes of the Americas, and the short-term Calumet stream data appear to refute that hypothesis. However, at Calumet the shallow soil water DON concentration was about 4 times that of DIN. The higher DON concentrations in shallow soil water could explain the increase in stream water DON concentration with discharge. The decline in stream water DOC/DON ratios with increased stream discharge indicated the quality of dissolved organic matter (DOM) improved with discharge. The quality improvement was the result of a relative gain in DON to DOC concentrations which likely reflected the increased movement of DON from shallow soil depths where its concentration was greatest ($\text{DON}/\text{DIN} = 4$, $p < 0.001$).

In the comparison of plot-level well water heights with stream water chemistry, the findings were limited because stream water represents an integration of terrestrial solute contributions from the entire watershed. And as earlier stated, stream water discharge is dominated by snowmelt runoff from the upper watershed for much of the hydrograph. The change in stream discharge source area to the upper watershed during snowmelt was likely a factor in the less tight relationship between well water height and stream water discharge than that shown for most solutes.

Using the relationship between well water heights and stream water solute concentrations, we attempted to estimate shallow lysimeter solute concentrations using the relatively conservative Cl^- . Cl^- was selected because its concentration changed the least between the forest floor and soil lysimeters, and forest floor inputs could be easily corrected for. However, because of the variable lag time between well water heights and stream water discharge, only weekly mean solute concentrations could be compared. Estimated and observed lysimeter Cl^- concentrations were correlated (coef. = 0.58, $p < 0.01$), but estimated values were significantly lower ($p < 0.001$). The greatest differences between estimated and observed lysimeter Cl^- concentrations occurred at high stream water discharge (well water heights $< 25 \text{ cm}$). As earlier stated, just prior to peak stream water discharge at the mouth the snowmelt hydrograph becomes dominated by runoff from the upper watershed

(Stottlemyer and Toczydlowski, unpub. data; Figure 1, station 2, especially sta 1). This condition persists through about two-thirds of the declining hydrograph limb.

The disparity between estimated and observed soil water solute concentrations again points out the limitation of attempting to describe watershed-level functions from plot-level processes. Other factors which might also account for the lack of comparable results would include use of tension soil lysimeters and the fact the change in the rising limb of the hydrograph is generally quite rapid limiting the number of stream water and soil solution samples that can be collected.

The relationships between stream and well water chemistry generally supported the results from the soil lysimeters. Chief among the findings were the positive correlations between stream and well water Ca^{2+} , NO_3^- , and DOC concentrations; and the inverse correlations between well water Ca^{2+} with well and stream water NO_3^- and stream water DOC concentrations (Table 3). However, there were some discrepancies that did not support soil and stream water linkage primarily the inverse relationship between stream water NO_3^- and well water DOC concentrations. But again the comparisons were between stream water chemistry, which reflected an integration of watershed-level processes, and essentially a point value (replicated plots) at near mid-elevation in the watershed. During much of the rising limb of the snowmelt hydrograph at Calumet, when watershed runoff is dominated by snowmelt from the lower portion of the watershed, both significant positive and inverse correlations between solute concentrations in soil, well, and stream water could be anticipated. However, once stream discharge becomes dominated by snowmelt and subsurface flow from the upper watershed, little, if any, correlation between stream and mid-elevation soil or well water solutes might be expected.

Watershed solute source area is a function of spatial extent and subsurface flow depth, and is affected by topography (Creed and Band 1998). A number of studies have shown the importance of flowpath depth in determining watershed output chemistry and flux (Mulholland et al. 1990; Ross et al. 1994; Mulholland and Hill 1997; Reuss et al. 1997). In an experimental study designed to increase shallow subsurface flow (Stottlemyer and Troendle 1999), a doubling of the percentage of total (1–4 m deep) subsurface flow occurring at shallow (<1 m) depths increased soil water K^+ and NO_3^- concentrations. The percentage of total Ca^{2+} , SO_4^{2-} , and HCO_3^- flux in shallow depths was less than the increased percentage of shallow subsurface flow, but K^+ and NO_3^- fluxes were greater. The present study also suggests that the character of the source area coupled with percent of runoff which occurs as shallow subsurface flow can be major factors accounting for trends in the winter solute concentration and flux. Our results also support other findings which show the importance of sub-catchment scale factors as presence of wetlands, vegetation, and soil impervious layers in affecting watershed outputs (Stottlemyer et al. 1998; Xenopoulos et al. 2003).

At Calumet, the relationship between stream solute concentration with discharge coupled with the correlation between soil (well) water height and stream water discharge provided further insight as to solute source areas (Tables 3 and 4). The concentration of most solutes in stream water was correlated with discharge (Table 4). As stream discharge increased, C_B , HCO_3^- , and Cl^- concentrations declined indicating dilution from increased snowmelt in near-surface lateral flow. The decline in concentration of most C_B and HCO_3^- also reflects their smaller available reservoirs in shallow soils, the result of long-term leaching by organic and carbonic acids. However, the concentration reductions with discharge were not one-to-one, and all solutes increased in output with discharge. In contrast with most C_B and HCO_3^- concentrations, stream water K^+ , SO_4^{2-} , DIN, DON, and DOC concentrations increased or showed no trend with greater stream discharge (Table 4).

There are numerous examples of significant concentration trends with time in surface water chemistry for streams, lakes, and rivers (Schindler et al. 1997; Martin et al. 2000; Worrall et al. 2004; Findlay 2005). However, as with the present study, most such studies were relatively short-term (< 20 years). Studies of similar length can also show a trend reversal in solute concentration and flux (Stottleyer et al. 1998; Goodale et al. 2003). Such reversals indicate caution should be used in linking cause-and-effect in accounting for trends in surface water solutes since longer-term yet unquantified factors will certainly be found.

In northern ecosystems, stream water DOC is the most abundant component of dissolved organic matter (DOM) discharged into lakes (Schindler et al. 1997). Aquatic DOC flocculates chemical substances, provides an energy source for the base of the aquatic foodweb, and reduces the aquatic penetration of photosynthetically active radiation (PAR). In the present study, the DOC concentration and flux was greatest in the forest floor leachate, a common finding in temperate hardwoods and conifers (Michalzik et al. 2001).

Other studies have observed long-term trends in river and stream DOC concentrations related to change in hydrology, warming temperature, and perhaps N deposition. Studies in the Experimental Lakes Area, Ontario, indicate decreased stream flow as the main cause of a decline in small lake DOC concentrations (Schindler et al. 1997). Increased DOC concentrations with time in rivers draining upland peatlands in the United Kingdom are common (Worrall et al. 2004). The concentration increase can not be fully accounted for by warming temperatures, and it is suspected increased soil decomposition rates are a factor. Other study implicates atmospheric DIN deposition as a factor possibly accounting for trends in river DOC concentration (Findlay 2005).

At Calumet the increase in stream water DOC concentration with discharge was greater since 1996. However, the ratio of DOC concentration to flux did not show any trend with time. This finding suggests that DOC flux was driven primarily by change in subsurface hydrology. During the study winter precipitation declined and runoff showed no trend (Figures 5 and 6) while DOC concentration and flux increased. Such results suggest that shifts in subsurface

lateral flow with depth were likely important. In earlier study at Calumet we found soil water DIN and DOC concentrations usually peaked when subsurface flow reached its shallowest depths and stream discharge peaked (Stottlemeyer and Toczydlowski 1999). As soil water levels became shallow and stream discharge increased, the outputs of DIN and DOC increased at a greater rate relative to base flow conditions than did the output of other solutes or stream discharge. Results from the earlier one-year study were supported by findings in the present study where DOC output was correlated with the amount of time subsurface flow was shallow, and the percentage of winter runoff and stream discharge that occurred during that time.

Freeman et al. (2001) hypothesize that a warming climate may increase DOC output from peatlands, while Tranvik and Jansson (2002) suggest that the effect of warming on DOC flux will depend on precipitation changes and links to hydrology. The present study gave results somewhat different from either Freeman et al. (2001) or Tranvik and Jansson (2002), and suggests that stream water DOC concentration and flux are also a function of the percentage of snowmelt runoff that moves laterally as shallow subsurface flow.

The present study did show warmer winter air temperatures than prior to 1988, but no trend within the study period. The soil temperature prior to snowpack formation and beneath the snowpack did increase with time especially after 1995 (Figure 3). However, winter soil temperatures remained < 2 °C, and field and laboratory studies suggest that DOC concentration is not that responsive to temperature (Pastor et al. 2003).

Since 1995, winter precipitation amounts and plot-level snowmelt showed their steepest declines at Calumet while winter stream water discharge was unchanged. Soil macropores are more prevalent at shallow depths and, coupled with the increase in number of days that shallow subsurface flow occurred, could account for why there was no decline in winter runoff after 1995. The rate that snowmelt occurred may also be a factor. Since 1995, only one year-1997-did not show the characteristic single large snowmelt hydrograph indicating rapid snowmelt at the watershed level. Also there was the time trend of increased snowmelt amount in the plot lysimeters just prior to peak stream water discharge. While there was no direct measurement of change with time in shallow subsurface lateral flow, the hydrologic results taken together suggest an increase during the study especially after 1995. Further evidence for this was the decline during the study in shallow soil lysimeter Ca^{2+} , Mg^{2+} , and SO_4^{2-} concentrations that suggests greater dilution from meltwaters.

DOC is a relatively mobile solute in shallow soils. This characteristic coupled with its high concentrations in forest floor and shallow soil solution and any increase in shallow subsurface flow could account for its time trend of increased stream water concentration and flux.

The increase in stream water DIN flux after 1995, almost all as NO_3^- -N, was also likely a response to the estimated increase in shallow subsurface lateral flow. NO_3^- is poorly adsorbed in soils and, with reduced winter retention by above- and below-ground biota, can form large mobile DIN

pools (12 kg N ha^{-1}) at Calumet (Stottlemeyer and Toczydlowski 1996a, b). In that study over-winter net N mineralization rates at Calumet were negative up to March and April when monthly rates became $> 1 \text{ kg N ha}^{-1}$. As discussed earlier, we could find no direct evidence of a change in soil nitrification rates that might be associated with frozen soils. Change in watershed retention rates associated with forest succession during the study do not seem likely either.

Of note also was the tighter relationship between stream water DIN concentration and discharge for the period 1996–2002 ($p < 0.01$, $r^2 = 0.30$, $b = 0.001 \text{ mg l}^{-1}$) relative to that in the longer time period 1988–2002 (Table 4). Prior to 1996, the Calumet snowmelt hydrograph was characterized by a number of increases and decreases in discharge particularly during the rising hydrograph limb (Stottlemeyer and Toczydlowski, unpub. data). With the exception of 2000, since 1996 at Calumet the rising limbs of the hydrograph in particular have been more uniform in shape. Stream water DIN concentration can have a much better relationship to discharge on the rising hydrograph limb than the falling limb especially when the rising limb is uniform in shape (Stottlemeyer and Troendle 1992).

Stream and well water $\text{NO}_3\text{-N}$ and DOC concentrations were strongly correlated. Total winter stream discharge, DIN, and DOC outputs were correlated with the percentage of stream discharge that occurred when subsurface flow was shallow (Table 7). Such results coupled with the evidence for an increase in shallow subsurface flow during the study, especially after 1995, would account for the increase in stream water DIN flux.

Solute flux, budgets

The decline in winter H^+ , DIN, and SO_4^{2-} inputs was primarily the result of a decrease in precipitation amount. For SO_4^{2-} inputs, the decline was also the result of decreased SO_4^{2-} concentrations from reduced SO_2 emissions in the eastern U.S. (Stottlemeyer and Toczydlowski 1996b). The linkage between precipitation amount and C_B inputs was less evident at NADP or Calumet stations. Precipitation chemistry from NADP event-collectors can be altered by local dust sources (Glass and Loucks 1986). The use of bulk collectors in winter at Calumet might further increase variation in precipitation chemistry especially for C_B owing to local dust inputs. The general decline in the time that snow covered the region during the study could also increase variation in C_B inputs.

The snowpack retained only a fraction of precipitation inputs up to snowpack PWE. The peak snowpack inorganic N content averaged about 60% of cumulative precipitation inputs up to that time. Our earlier studies at Calumet showed that snowpack temperatures (10 and 40 cm above the forest floor O2 layer) are sufficient for solute migration into snow lysimeters throughout most of winter, but the melt volume is small (Stottlemeyer and Toczydlowski 1996b, 1999). The small gain in snowpack DOC content relative to precipitation

inputs (Table 5) we attribute to canopy drip from snowfall retained by leaf-free hardwoods, and the leaching of organic debris in the snowpack similar to that observed for snowpack K^+ content (Hornbeck and Likens 1974; Stottlemeyer and Toczydlowski 1996b).

At Calumet the snowpack PWE inorganic N content averages 10–20% of the inorganic N pool size in the top 10 cm of the forest floor O2 (Stottlemeyer and Toczydlowski 1996a). While some atmospheric inorganic N input must directly reach the stream during snowmelt, the amount was small based upon our N budget estimates. This finding is consistent with results from a variety of small watersheds with a range of atmospheric N inputs (Kendall et al. 1995).

Winter stream water solute outputs showed little or no response to the change in runoff during 1995–2002 (Figure 5). Despite a leveling off of the decline in winter runoff after 1995, the runoff/precipitation ratio did not change. Lowess plots of Ca^{2+} winter output showed little change in the rate of decline after 1995 and linear models showed no significant change in slope. This suggests that the ratio of deeper soil water contributions to total watershed solute outputs declined.

Stream water DIN output increased >40% during the study despite a 50% decline in winter DIN inputs since 1988. DIN inputs declined 0.8 kg N ha^{-1} and outputs increased $0.15 \text{ kg N ha}^{-1}$, a net difference of about 1 kg N ha^{-1} during the 16 winters. This is a small amount relative to available winter inorganic N pools (Stottlemeyer and Toczydlowski 1996a). Lowess and regression analyses showed no trend in winter DIN output up to 1995 then an increase in output ($p = 0.01$, $r^2 = 0.60$, $b = 0.03 \text{ kg N ha}^{-1}$) each winter for 1995–2002.

Winter stream water DOC output increased 7 kg ha^{-1} during the study. This amount too was a small increase relative to the estimated annual flux beneath the forest floor and shallow mineral soils of the mid-elevation plots (Table 5). The Lowess analyses of the time trend indicated an increase in DOC output during 1994–2002, but the slope change was not significant from 1988–1994. The absence of significant time trends in winter output for most other solutes (Table 6) we attribute to the short study period and high variation in winter runoff (Figure 5).

In earlier study at Calumet we found winter watershed DIN retention >90%, and that total dissolved nitrogen (TDN), phosphorus, and DOC outputs peaked when soil solution levels approached the forest floor (Stottlemeyer and Toczydlowski 1996b, 1999). With the longer record (16 winters) in the current study, we can better quantify the relationship between the length of time shallow subsurface lateral flow in the plots occurred near or within the forest floor and winter watershed solute flux.

As stated earlier, during the study the number of days that shallow (<25 cm beneath Oi) subsurface lateral flow occurred ranged from 2 to 17. As the length of time and percent of winter runoff during shallow subsurface flow increased, DIN and DOC outputs increased while other solutes declined or showed no trend (Table 7). This finding suggests the presence of large

dormant-season forest floor solute reservoirs that were not quickly depleted. In the Lake Superior region, dormant season N mineralization rates and soil inorganic N pools in the forest floor can exceed non-winter averages which likely accounts for why winter stream water DIN and DOC concentrations are usually higher than in other seasons (Foster et al. 1989; Stottlemyer et al. 1998).

The present study suggests the need to use time trends for a suite of stream solutes to better identify possible mechanisms accounting for why watershed outputs and solute concentrations may, at least in the short term, vary in ways not expected in a warmer and drier climate. Lewis (2002) and others have shown that N fractions in watershed exports are strongly related to runoff over a wide latitudinal range. The Calumet study suggests that the percentage of annual runoff occurring as shallow subsurface flow may also be a major factor regulating output of DIN, DOC, and likely DON in snowmelt-dominated watershed ecosystems. Change in shallow subsurface hydrology, likely the result of trends in watershed-level snowmelt rates associated with warming air and soil temperatures, could also account for time trends or shifts in stream solute concentrations. While most of the increase in stream water NO_3^- and DOC concentrations with time in this study were not especially strong ($r^2 = 0.17\text{--}0.47$), the trends were present for much of a 16-year period, particularly during the last decade, and appeared independent of atmospheric and snowmelt inputs. It is possible similar shifts in dominant subsurface flowpath in response to altered precipitation and snowmelt rates might also account for changes with time in stream water DIN concentrations observed in other studies (Goodale et al. 2003).

Conclusions

During the past two decades, change in weather patterns along the south shore of Lake Superior resulted in warmer and drier winters with less snowmelt runoff. The weather shifts brought about warmer soils prior to snowpack formation, and a reduction in time a snowpack was present. Winter atmospheric inputs of most solutes, in particular H^+ , NO_3^- , NH_4^+ , DIN, and SO_4^{2-} , declined as did snowpack PWE solute content.

Despite a trend of declining winter runoff associated with snowmelt, plot-level results suggested the percentage of total winter runoff that occurred as shallow (<25 cm) subsurface flow increased. This increase was concurrent with divergent patterns in stream water solute concentration and outputs. More mobile solutes with higher concentrations in shallow soils, NO_3^- , DOC, DON, generally increased in stream water concentration and output with increased shallow subsurface flow while solutes associated with deeper soils, as represented by the C_B , declined or showed no trend. The divergent flux and concentration patterns were more evident for the period 1995–2002 than for

1988–1995. But the cause for this could not be fully explained in this relatively short-term study.

In general, the mid-elevation replicated plot-level results supported observations at the watershed level, but also demonstrated that plot-level studies without extensive spatial replication can not be directly applied in quantifying cause and effect for variation in solute flux at the watershed-level. Major hydrologic limitations in linking the plot-level studies to the watershed-level were (1) the variable time lag in soil water levels relative to stream discharge rates during the rising hydrograph, and (2) the shift in stream water source area to the upper watershed just prior to peak snowmelt runoff.

The study further documented the high year-to-year variation in hydrology and solute flux characteristic of small, snow-dominated watershed ecosystems. To quantify the mechanisms causing change in stream water solute export and concentration in response to climate change would require long-term study, a major increase in the intensity of plot-level study, and use of natural abundance isotopes.

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