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Effects of a beaver pond on runoff processes: comparison of two headwater catchments

Douglas A. Burns[a,*], Jeffrey J. McDonnell[b]

[a]*US Geological Survey, 425 Jordan Rd., Troy, NY 12180, USA*
[b]*SUNY College of Environ. Sci. and Forestry, 1 Forestry Dr., Syracuse, NY 13210, USA*

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Abstract

Natural variations in concentrations of ^{18}O, D, and H_4SiO_4 in two tributary catchments of Woods Lake in the west-central Adirondack Mountains of New York were measured during 1989–91 to examine runoff processes and their implications for the neutralization of acidic precipitation by calcium carbonate treatment. The two catchments are similar except that one contained a 1.3 ha beaver pond. Evaporation from the beaver pond caused a seasonal decrease in the slope of the meteoric water line in stream water from the catchment with a beaver pond (WO2). No corresponding change in slope of the meteoric water line was evident in stream water from the other catchment (WO4), nor in ground water nor soil water from either catchment, indicating that evaporative fractionation was not significant. Application of a best-fit sine curve to $\delta^{18}O$ data indicated that base flow in both catchments had a residence time of about 100 days. Ground water from a well finished in thick till had the longest residence time (160 days); soil water from the O-horizon and B-horizon had residence times of 63 and 80 days, respectively. Water previously stored within each catchment (pre-event water) was the predominant component of streamflow during spring snowmelt and during spring and autumn rainfall events, but the proportion of streamflow that consisted of pre-event water differed significantly in the two catchments. The proportion of event water (rain and snowmelt) in WO2 was smaller than at WO4 early in the spring snowmelt of March 13–17, 1990, but the proportions of source water components for the two catchments were almost indistinguishable by the peak flow on the third day of the melt. The event water was further separated into surface-water and subsurface-water components by utilizing measured changes in H_4SiO_4 concentrations in stream water during the snowmelt. Results indicated that subsurface flow was the dominant pathway by which event water reached the stream except during the peak flow of a rain-on-snow event on the last day of the melt. Streamflow from a spring rain storm with dry antecedent conditions two months later (May 16–18, 1990), was less than 5% event water at peak flow in WO2 and 26% in WO4. This change from the runoff pattern in March is attributed to retention of event water in the beaver pond favored by relatively low pre-event storage and isothermal (nonstratified) conditions in the pond that allowed mixing. Streamflow during several autumn storms was about 15–25% event water at peak flow in WO4; the highest values for event water were associated with wet antecedent moisture conditions. These results indicate that a beaver pond can significantly affect the downstream delivery of event water through evaporation and mixing, but provides minimal retention during large runoff events such as snowmelt. Beaver ponds are expected to provide greater opportunity for neutralization of acidic waters during most of the year in catchments treated with calcium carbonate, but little neutralization effect during snowmelt.

Keywords: Storm runoff; Snowmelt; Isotopic tracers; Beaver ponds; Groundwater dating; Evaporation

* Corresponding author.

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1. Introduction

Analysis of the natural variations in the isotopic composition of precipitation, ground water, and stream water can provide information on a wide variety of hydrologic processes within a watershed, including: evaporation, subsurface residence time of water, and the source-water components of stormflow (Kendall et al., 1995). Isotope data can also be combined with surface-water chemistry data to suggest runoff mechanisms and indicate the dominant hydrologic flowpaths during rainfall or snowmelt (Wels et al., 1991). The stable isotopes of water ($\delta^{18}O$ and D) in precipitation and streamflow were first used in the 1970s to separate hydrographs into their runoff components (Dincer et al., 1970; Martinec et al., 1974; Sklash et al., 1976). The results indicated that stormflow consisted mainly of pre-event water—water that resided in the catchment prior to rainfall or snowmelt—in contrast to the results obtained from traditional hydrograph separations by graphical methods (Hursh and Brater, 1941), which indicated that stormflow consisted mainly of event water (precipitation). The predominance of pre-event water in stormflow has now been established in a wide variety of catchments and runoff environments mainly in temperate, humid climates (Sklash, 1990; Buttle, 1994), and recent research has focused on (1) defining the mechanisms by which pre-event water reaches streams (Abdul and Gillham, 1989; McDonnell, 1990), and (2) refining modeling approaches for the application of isotope data to runoff production (DeWalle et al., 1988; Harris et al., 1995). Recent work has emphasized the contribution of soil water to stormflow and has highlighted the inadequacy of using two-component (event and pre-event water) models alone to evaluate runoff components (Mulholland, 1993; Ogunkoya and Jenkins, 1993; Brown et al., 1997).

Natural variations in the concentration of chemical constituents have also been widely used to separate stream hydrographs into runoff components (Pinder and Jones, 1969; Kennedy, 1971), often in conjunction with isotopic analyses (Wels et al., 1991; Ogunkoya and Jenkins, 1993). A principal difference between the two approaches is that chemical constituents derived from the subsurface are potentially reactive and may not mix conservatively, whereas stable isotopes such as ^{18}O and D can generally be assumed to be transported conservatively in the absence of significant evaporation. Therefore, the results of a hydrograph separation based on isotopic data could differ from the results of a separation based on chemical data. If the reaction kinetics of a given chemical constituent in the subsurface are well known, however, isotopic and chemical hydrograph analysis can be complementary and provide more detailed information about runoff components and source water flowpaths than either method could provide alone (Wels et al., 1991).

Although separation of a runoff hydrograph helps to quantify the stormflow components, it provides little information on the residence time of pre-event waters in the catchment before they discharge to the stream. Cyclic variations of ^{18}O and D in precipitation and catchment waters have been modeled through techniques such as time-series analysis and solution of the convolution integral to determine catchment residence time at sites where traditional age-dating methods such as tritium are inadequate (Maloszewski et al., 1983; Turner and Macpherson, 1990; Stewart and McDonnell, 1991). A recent review of runoff processes concluded that further studies that focus on the residence time of waters are needed to extend our interpretation of catchment hydrology beyond the simple two-component paradigm (Bonell, 1993).

This paper describes a study to quantify source water components and flowpaths in two tributaries to a small lake in the Adirondack Mountains of New York. The study site was at Woods Lake, a catchment where the processes that affect lake acidification in the Adirondack region have been studied since 1977 (Goldstein et al., 1985). More recently, Woods Lake has been the location of studies of lake and lake catchment neutralization through calcium carbonate application (Porcella, 1989; Driscoll et al., 1996). Early work concluded that runoff in the Woods Lake catchment was dominated by surface runoff and shallow interflow, explaining in part, why Woods Lake was more acidic than nearby Panther Lake which is underlain by similar bedrock but with thicker till (Peters and Murdoch, 1985). One objective of the lake catchment liming study was to determine the effectiveness of the treatment in neutralizing precipitation acidity during periods of high flow from rain and snowmelt (Driscoll et al., 1996). Calcium carbonate was applied to the

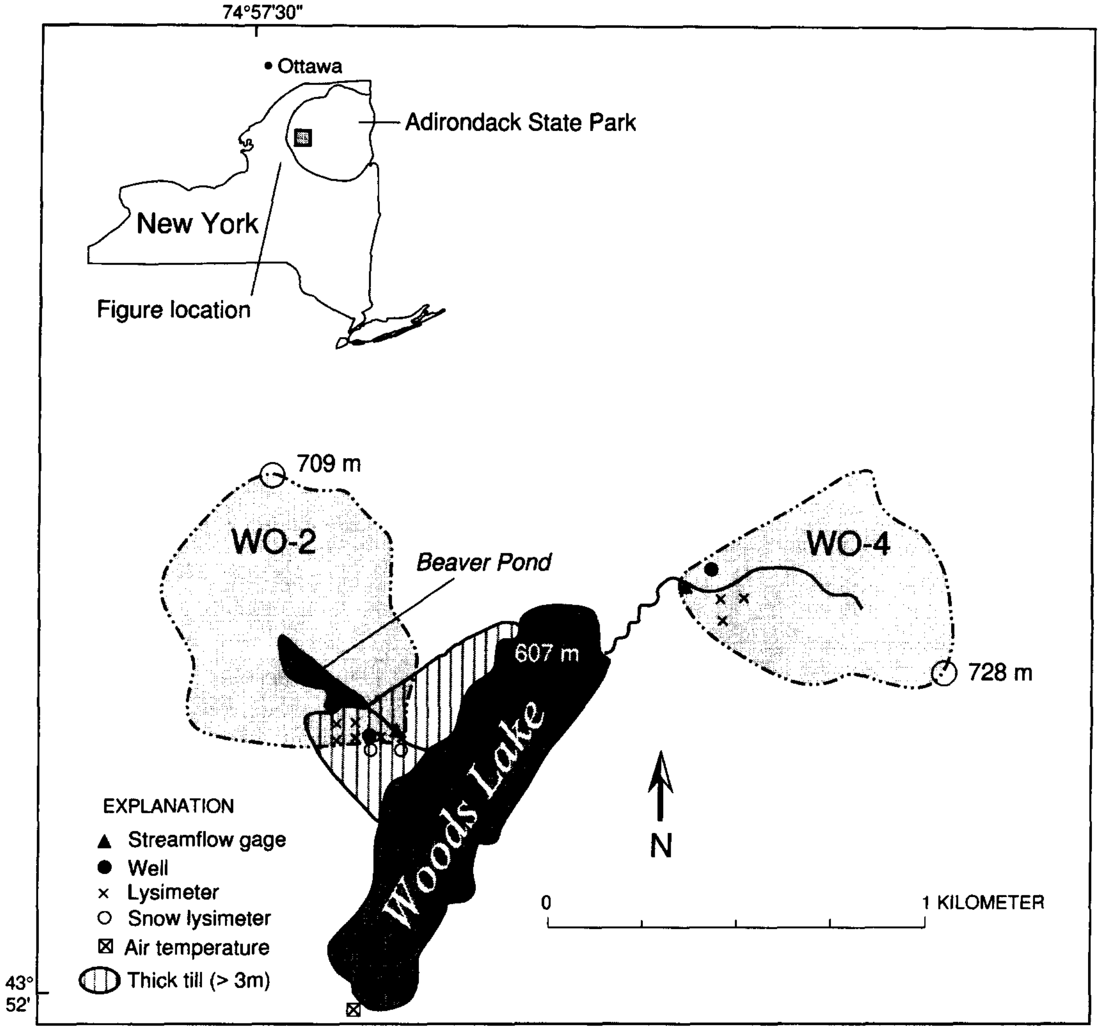

Fig. 1. Map of Woods Lake with the gaged areas of catchments WO2 and WO4 shown. Locations of the wells, soil-water lysimeters, snow lysimeters, and air temperature probe are also shown on the map.

catchments of the two tributaries used in the present study. The two catchments are similar, except that one contains a beaver pond (Fig. 1). Beaver ponds are known to alter the hydrologic regime in watersheds (Johnston and Naiman, 1987; Woo and Waddington, 1990), and to affect the chemistry of drainage waters (Naiman et al., 1994; Cirmo and Driscoll, 1996); thus, response to calcium carbonate treatment in the catchment with a beaver pond was expected to differ from that in the catchment without a beaver pond. The objective of the present study was to compare these two catchments through isotopic and chemical-tracing techniques during low- and high-flow conditions and to identify underlying hydrological mechanisms for potential use in future applications of lime to lake catchments in the region. This paper presents: (1) a discussion of the extent of evaporation from the beaver pond through analysis of $\delta^{18}O$ and D meteoric water lines, (2) an estimate of the mean catchment residence time of the two streams at base flow through a comparison of seasonal fluctuations in $\delta^{18}O$, and (3) a comparison of the source water components and flowpaths of the two streams during snowmelt and rain events during selected seasons through hydrograph

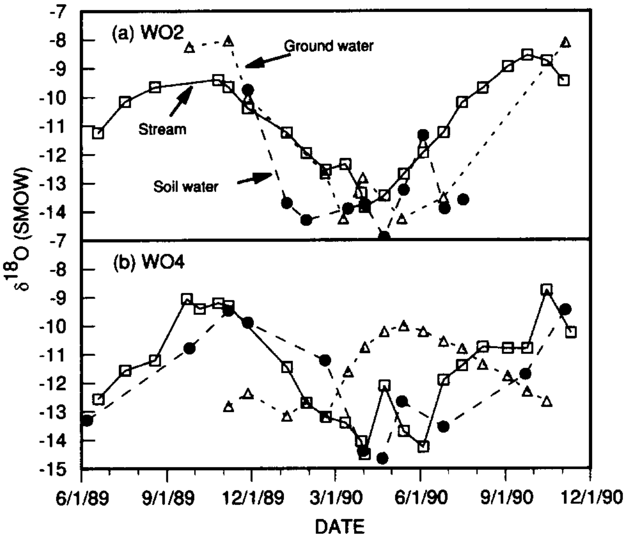

Fig. 2. $\delta^{18}O$ data for base flow, soil water, and ground water, 1989–90: (a) WO2; (b) WO4.

separations as indicated by $\delta^{18}O$ and H_4SiO_4 concentrations in the stream waters.

2. Site description

Woods Lake (43°52′N, 74°58′W) is a 25 ha, chronically acidic lake (pH 4–5) in the west-central Adirondack region of New York State (Fig. 1). The lake catchment drainage area (excluding the lake) is 181.6 ha, and the lake is fed by the two tributaries studied—a perennial stream on the west side (WO2), which contains a beaver pond and has a drainage area of 41.3 ha, and an ephemeral stream on the northeast side (WO4), which has a drainage area of 61.2 ha and no beaver pond. Calcium carbonate pellets were applied by helicopter to the catchments of WO2 and WO4 in October 1989 at a rate that varied from 5000 to 10 000 kg ha^{-1}. Further details of the catchment treatment and the response of stream and lake chemistry are given in Driscoll et al. (1996).

The Woods Lake catchment is forested and hilly and is underlain by sandy till with a mean thickness of 2.3 m, interspersed with outcrops of granitic gneiss (April and Newton, 1985). A discontinuous mantle of aeolian silt up to 0.5 m thick with low hydraulic conductivity overlies the till in places, and an area of thick till (>3 m) underlies about 10% of the catchment (April and Newton, 1985). The area of thick till parallels the northwest shore of the lake and includes the lower part of the catchment of WO2 (Fig. 1). The well sampled in the catchment of WO2 is in the thick till area, whereas the well in the catchment of WO4 is in the thin till area. The soils are classified generally as spodosols with a thick O-horizon (100–200 mm), a heavily leached E-horizon, and a distinctive B_{hs} (spodic) horizon that is enriched in organic matter (Cronan, 1985). The catchment of WO2 contains a 1.3 ha beaver pond that was impounded in 1988, and a wetland area of about 1.1 ha adjacent to the lake (Cirmo and Driscoll, 1996). The till in the area of the wetland and beaver pond is covered by 0.25–1500 mm of peat.

The region has a humid, continental climate with cold, snowy winters and mild summers. Mean annual air temperature is 5.2°C, and the annual range is generally from −40 to 27°C. Mean annual precipitation is 1180 mm, of which 490 mm falls as snow (1961–90; National Weather Service). Evapotranspiration is equivalent to about 40% of annual precipitation (Peters and Murdoch, 1985). Streamflow in the region is dominated by the spring snowmelt, which typically occurs between mid-March and mid-April, when about one-third of the annual discharge occurs.

3. Methods

3.1. Field

Streamflow in the catchments of WO2 and WO4 was recorded every 15 min with Parshall flumes from November 1988 through October 1990. Air temperature was recorded every 15 min with a thermistor probe near the Woods Lake outlet. The gaged drainage areas were 30.6 ha at WO2 and 17.2 ha at WO4, considerably less than the entire drainage area of each stream (Fig. 1). Stream-water samples were collected at the gage sites for isotopic and chemical analysis, and ground-water samples were collected from a single well in each catchment. The well in the catchment of WO2 was made of 102 mm ID, Schedule 40 PVC, and was installed about 15 m from the stream channel at a depth of 2300 mm in till, screened from the bottom to a depth of about 1920 mm. The well in catchment WO4 was made of the same material and installed 60 m from the stream channel at a depth of 820 mm in till, and screened from the bottom to a depth of 440 mm. The screened area of each well encompassed the water table at low flow conditions in the summer of 1989. Soil water was collected from five zero-tension lysimeters in the catchment of WO2 and three zero-tension lysimeters in the catchment of WO4 (Fig. 1). These lysimeters consisted of square polyethylene containers about $150 \times 150 \times 30$ mm filled with pure quartz sand that drained into a 2 l polyethylene bottle. At each lysimeter site, three or four lysimeter containers were placed immediately below the soil O-horizon at depths that ranged from about 80 to 120 mm, and a second set of containers placed in the soil B-horizon at a depth of about 300 mm. Snowmelt samples were collected from two 1220×910 mm rectangular PVC snow lysimeters placed about 10 m from each other on the forest floor in late fall.

Water samples were collected from the streams and the wells at base flow every 3 weeks. The lysimeters were sampled every 3 weeks on a rotating basis such that each lysimeter was sampled every 6 weeks. Stream samples were collected during rainstorms and snowmelt in 1 l polyethylene bottles by an automated water sampler programmed to collect samples as stream stage rose and fell. Precipitation samples were collected in a wetfall/dryfall collector at Big Moose, NY, about 10 km E of Woods Lake. Grab samples were collected in 60 ml glass bottles with caps that had plastic conical inserts that seal to prevent evaporation. Event stream-water samples and precipitation samples were transferred to glass bottles in the laboratory, and were then shelf stored at room temperature until shipped for isotopic analysis.

3.2. Laboratory

Concentrations of the stable isotopes ^{18}O and D were measured in base-flow, ground-water, and soil-water samples. High-flow stream-water and precipitation samples were analyzed only for ^{18}O. Isotope samples were analyzed by mass spectrometry at the US Geological Survey Stable Isotope Laboratory in Reston, VA. Values are reported in per mil (‰) units relative to Vienna Standard Mean Ocean Water (VSMOW) and normalized to scales in which the oxygen and hydrogen isotope values of Standard Light Antarctic Precipitation are −55.5 and −428‰, respectively (Coplen, 1988). The precision (2 × std dev.) of oxygen and hydrogen isotope results are 0.1 and 1.5‰, respectively. Additionally, high flow stream-water samples were analyzed for dissolved H_4SiO_4 according to methods described in Driscoll et al. (1996).

3.3. Modeling

3.3.1. Base flow

Seasonal changes in the $\delta^{18}O$ composition of precipitation at temperate latitudes tend to follow a sinusoidal pattern with a period of one year reflecting the seasonal changes in tropospheric temperature (Maloszewski et al., 1983). Monthly precipitation $\delta^{18}O$ values were estimated from monthly mean air temperature using the following linear regression derived from 9 years of data collected at Ottawa, Ontario (International Atomic Energy Agency, 1981), about 150 km north of Woods Lake: $\delta^{18}O = (0.23 \times \text{temp.}) - 13.25$; $r^2 = 0.71$. Measured changes in $\delta^{18}O$ of stream-water, ground-water, and soil-water at Woods Lake similarly followed a sinusoidal pattern during the study period (Fig. 2). Assuming that these waters represent a steady-state, well-mixed reservoir with an exponential distribution of residence times (Eriksson, 1958), the mean catchment residence time of each of these waters can be calculated through a comparison of the amplitude of a best-fit sine curve for precipitation to the amplitude of a similar curve for the water of interest (stream water, ground water, or soil water), as follows:

$$T = \omega^{-1}[(A/B)^2 - 1]^{1/2} \quad (1)$$

where T is the residence time (days), ω the angular frequency of variation ($2\pi/365$ days), A the input amplitude, and B the output amplitude.

3.3.2. High flow

A mass-balance expression was solved for each catchment to determine the contributions of event and pre-event water to streamflow at each time for which $\delta^{18}O$ analyses were available for stream water:

$$Q_sC_s = Q_pC_p + Q_eC_e \quad (2)$$

where Q is the volume, C the concentration of the tracer, and the subscripts s, p, and e refer to the stream, pre-event water, and event water, respectively. The concentration of tracer in pre-event water (C_p) was determined from a sample of stream water collected before the onset of an event, and the concentration of tracer in event water (C_e) was determined from a bulk sample of the precipitation or melting snow.

Isotopic tracers provide no information about how event water and pre-event water enter the stream channel unless additional hydrometric or tracer data are available. The use of isotope data alone to define hydrologic flowpaths has resulted in widely varying proposed mechanisms to explain the large proportion of pre-event water that constitutes most event hydrographs (Buttle, 1994). Chemical tracers such as H_4SiO_4 provide more information than isotopes about hydrologic flowpaths if the kinetics of tracer reactivity in the subsurface are well known (Wels et al., 1991). For example, in the spodosol soils of the Woods Lake catchment, Si dissolves readily as water enters the subsurface; therefore, the H_4SiO_4 concentrations of O- and B-horizon soil waters are similar to those of base-flow stream water (Geary and Driscoll, 1996), and because precipitation and melting snow contain little dissolved H_4SiO_4 (0–2 μmol l^{-1}), a hydrograph separation based on H_4SiO_4 concentrations will divide streamflow into surface-water and subsurface-water components (Maulé and Stein, 1990; Wels et al., 1991). Thus, combining the isotopic- and chemical-tracer approaches to separate a hydrograph will divide the event water component (Q_e) into two additional components—Q_{es} (event surface water) and Q_{ess} (event subsurface water) as follows:

$$Q_sC_s = Q_pC_p + Q_{es}C_{es} \quad (3)$$

where subscripts, s, p, and es are the same as defined previously. The quantities C_p and C_{es} were determined from samples of pre-event stream water and precipitation or melting snow, respectively. Because Si dissolves rapidly in the subsurface, $Q_{es} < Q_e$, and Q_{ess} is determined by:

$$Q_{ess} = Q_e - Q_{es}. \quad (4)$$

The Q_{es} component is not analogous to overland flow, but rather is water transported to the stream without dissolving any silica along its path.

4. Results

4.1. Meteoric water lines

The local meteoric water lines for streams WO2 and WO4 (Figs. 3(a) and (b)) have similar slopes and y-intercepts ($p > 0.05$), but there is more scatter about the regression line for WO2 than that for WO4. If separate least-squares regression lines are fit to the fall–winter 1989–90 isotopic data and the spring–summer 1990 isotopic data from WO2, two relations become evident (Fig. 3(c))—the line for the fall–winter data has a slope of 7.64, whereas the line for the spring–summer data has a slope of 6.90. This divergence reflects the effects of evaporation from the beaver pond on the isotopic composition of WO2 (the slopes are significantly different; $p < 0.01$). Evaporation is a nonequilibrium process that enriches D less than ^{18}O in the remaining water such that the slope of the D–^{18}O relation decreases from about 8 (global meteoric water line) to a range of 3–6 (International Atomic Energy Agency, 1983). Evaporation from the beaver pond in the Woods Lake climatic regime was sufficient to decrease the slope of the meteoric water line by less than 1. The data from WO4 do not show a similar seasonal shift, providing further indication that the shift in WO2 is due to evaporation from the beaver pond.

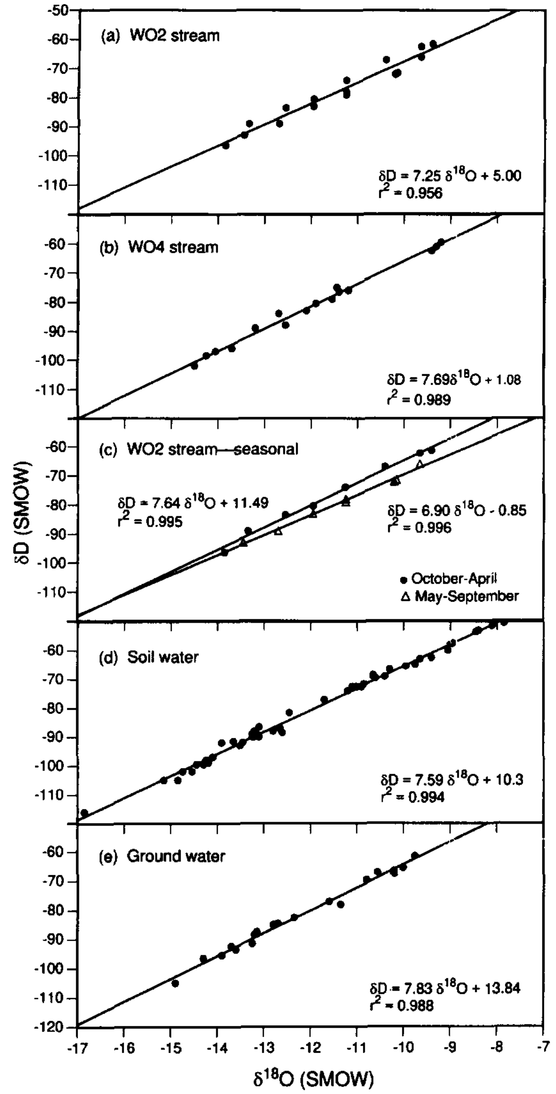

Fig. 3. δD data as a function of $\delta^{18}O$ data from the study catchments, 1989–90: (a) stream WO2; (b) stream WO4; (c) stream WO2 by season; (d) soil water; (e) ground water.

The similar slopes and y-intercepts of the meteoric water lines for all soil-water samples (Fig. 3(d)), all ground-water samples (Fig. 3(e)), and all stream-water samples suggests that these three different water types are closely related. Similarly, no significant seasonal differences were noted among the meteoric water lines for soil-water or ground-water samples in the two catchments. The summer evaporative fractionation observed in stream-water samples from WO2 was not evident in the ground-water or soil-water samples indicating that evaporation does not greatly affect subsurface waters.

4.2. *Seasonal variability at base-flow conditions*

The $\delta^{18}O$ values of base-flow samples from WO2 and WO4 were compared with estimated $\delta^{18}O$ values of local precipitation. Results indicate that the $\delta^{18}O$ of both streams follows a generally sinusoidal pattern that reflects seasonal changes in precipitation (Fig. 4). If precipitation had been collected locally and analyzed for $\delta^{18}O$ during the study period, the data probably would have shown more scatter than the Ottawa-based estimates, but would have followed the same seasonal pattern.

Seasonal changes in $\delta^{18}O$ of the two streams lag slightly behind the seasonal changes in precipitation with lower amplitude, suggesting that both mixing and storage are affecting the composition of stream water. Both streams reached their minimum $\delta^{18}O$ value in early April 1990, several months after the estimated minimum $\delta^{18}O$ value for precipitation. This is likely because most of the winter precipitation at this site is snow, and is stored in the snowpack until spring snowmelt, resulting in the observed lag between $\delta^{18}O$ changes in precipitation and stream water. The maximum $\delta^{18}O$ value in both streams was reached in the fall of 1989 and 90, 2–3 months after the maximum $\delta^{18}O$ value in precipitation, suggesting either a lag caused by mixing and storage, or that little of the summer rain contributed to ground-water recharge and, thus, was not a component of base flow.

The $\delta^{18}O$ values from WO2 exceed those from WO4 in the summer. The $\delta^{18}O$ values of the two streams are similar through the fall and winter, then begin to diverge in May, and converge again in October. This seasonal pattern can be attributed to evaporation from the beaver pond in the catchment of WO2 which causes $\delta^{18}O$ to increase more than in WO4.

Comparison of the seasonal changes in $\delta^{18}O$ of stream water and soil water in WO2 and WO4, and ground water in catchment WO2 indicates that all three types of water followed the same seasonal pattern—values were lowest in the early spring and increased until the early fall (Fig. 2(a)), although some

Table 1
Mean residence time of waters in the Woods Lake study catchments for the period June 1989 through October 1990

Water type	Mean residence time (days)	Adjusted r^2 for fit of sine function to data
WO2 stream water	102	0.95
WO4 stream water	103	0.81
B-Horizon soil water	80	0.86
O-Horizon soil water	63	0.80
WO4 ground water	160	0.87

notable differences are apparent. For example, the ground water at WO4 reached its greatest $\delta^{18}O$ value in May 1990 when the $\delta^{18}O$ value of stream and soil water were still near their minimum values for the year, and reached its lowest $\delta^{18}O$ value in the fall, when the stream and soil water were near their maximum. This difference suggests that the seasonal response of ground water from this well lags behind the response of stream water because the sampled ground water has a greater residence time than base flow and soil water. Ground water at the depth and location of this well is not representative of the predominant source of base flow in WO4, and would not reliably represent pre-event water in a hydrograph-separation model for this catchment.

Application of the relation described in Eq. (1), indicates base flow in both WO2 and WO4 had similar mean residence times of about 100 days during the study (Table 1). Soil water from the O-horizon (mean value for all lysimeters) had a mean residence time of 63 days, and soil water from the B-horizon had a mean residence time of 80 days, whereas ground water from the well in the catchment of WO4 had a mean residence time of 160 days, significantly greater than that of the stream, as expected from the response lag mentioned previously (Fig. 4(b)). A complete year of data was not obtained from the well in the catchment of WO2, and the pattern of seasonal changes was too erratic to fit a sine function to the data, so the residence time of the WO2 ground water was not calculated. Overall, these data indicate that waters in the Woods Lake catchment are relatively young, which is consistent with conclusions from an earlier study that the subsurface residence time of ground

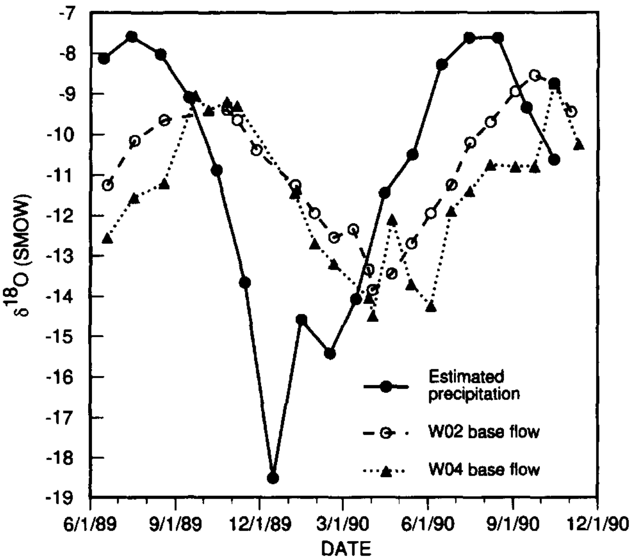

Fig. 4. $\delta^{18}O$ data for base flow samples collected from WO2 and WO4, and estimated $\delta^{18}O$ of composited monthly precipitation.

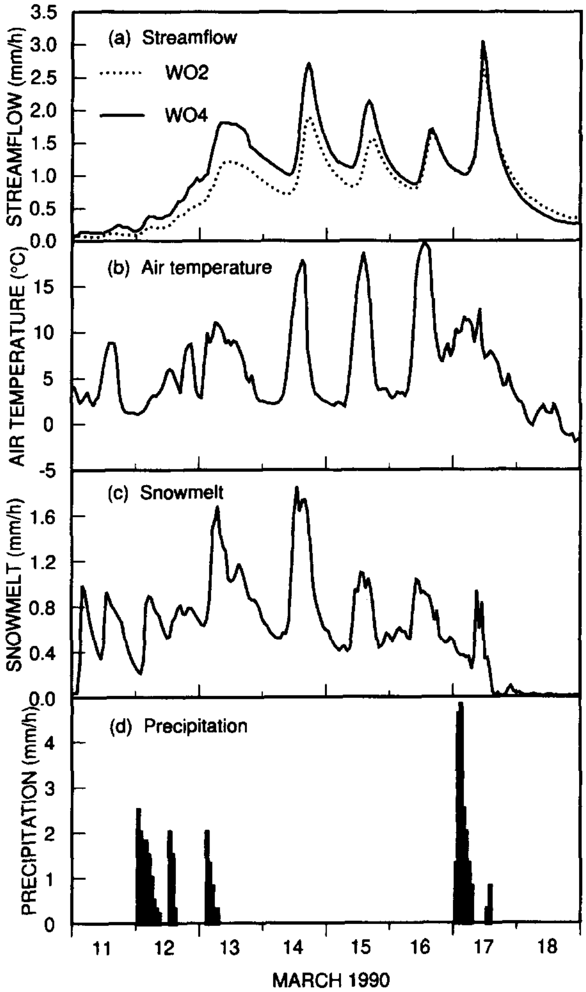

Fig. 5. Hydrologic data for March 1990 snowmelt: (a) discharge of streams WO2 and WO4; (b) air temperature from a site on the Woods Lake outlet stream; (c) rate of snowmelt from the snow lysimeter in catchment WO2 (the snowpack was gone from the lysimeter by noon on March 16; thus the lysimeter served as a throughfall collector thereafter); (d) hourly precipitation.

water that contributed to the lake is inadequate for complete neutralization of the acidity in precipitation (Peters and Murdoch, 1985). These data also indicate that, despite the beaver pond in the catchment of WO2, the residence time of base flow is similar in both catchments. These results are not surprising, considering that the beaver pond occupies only about 4% of the catchment area and has a turnover time of 6–31 days at the typical base-flow discharge range of 2.8–14 l s^{-1}. If stream water did not completely mix within the pond, the turnover time would be even less.

4.3. *High flow conditions*

4.3.1. *Spring snowmelt (March 1990)*

4.3.1.1. Hydrological data. An extended period of warmer-than-normal air temperatures during March 11–18, 1990, melted most of the winter's snowpack and resulted in a series of diurnal runoff peaks during March 13–17 (Fig. 5(a)). The runoff period was unusual for spring snowmelt because much of it (March 14–16) was rain-free (Fig. 5(d)). A total of 20 mm of rain fell and the snow lysimeter recorded about 41 mm of meltwater at the base of the snowpack on March 12 and 13. Stream discharge increased gradually through March 12 and reached a peak on the morning of March 13. No additional precipitation occurred until the early morning of March 17, when 18 mm of rain fell. The mean daily air temperatures during the melt period ranged from 0.5 to 9.4°C, and remained above freezing until March 18 at 5:00 a.m. A strong relation between air temperature and stream discharge at WO2 and WO4 was evident during the period from March 13 through the morning of March 16 (Fig. 5(a) and (d)), after which the snowpack at the snow lysimeter was gone and only patchy snow cover remained throughout both catchments. Stream discharge on March 17 was related to rainfall intensity and not directly related to air temperature (Figs. 5(a) and (d)).

A water budget calculation indicates that the total amount of precipitation and snowmelt in each catchment during March 11–17 was less than runoff during March 11–18. A snow survey on March 10 indicated that 148 mm of water was stored in the snowpack, and an additional 38 mm of rain had fallen by March 17. Runoff during March 11–18 was 177 mm at WO4 (95% of total precipitation) and 135 mm at WO2 (73% of total precipitation). The high proportion of precipitation and snowmelt that exited each catchment as streamflow during the melt period is due to the small amount of sustained ground water storage available in the Woods Lake catchment—a reflection of the thin till that underlies most of the catchments of WO2 and WO4 (April and Newton, 1985; Peters and Murdoch, 1985). Additionally, the aeolian silt with low saturated hydraulic conductivity values (April and Newton, 1985) may cause perching of ground water and a more rapid discharge to the streams. The difference in the proportion of precipitation that exited each catchment as runoff may be partly due to storage in the beaver pond, and partly due to storage in the thicker till in the catchment of WO2.

4.3.1.2. Hydrograph separations. The snowmelt period was treated as two separate events—the snowmelt during March 13–16, and the rain-on-snow during March 17. The pre-event water component was calculated from base-flow samples collected on March 12, just before streamflow began to increase, and the resulting value was applied throughout the entire March 13–17 period. The event water component was applied as two different subcomponents—the mean of two bulk snowmelt-lysimeter samples collected on March 14 to represent all melting that had occurred up to that time, and a bulk rain sample collected from the March 17 event. Ideally, samples of melting snow would have been collected more frequently to encompass the range of $\delta^{18}O$ values; other studies have shown that snowmelt tends to have its lowest $\delta^{18}O$ values early in the melt period, then becomes enriched as the pack melts (Stichler, 1987; Maulé and Stein, 1990). Rapid melting over a short period, such as occurred in this study, however, should result in a relatively small fractionation of the melting snowpack (Maulé and Stein, 1990). The effect of a changing $\delta^{18}O$ value in snowmelt on the separation of streamflow into event and pre-event water components was examined through a sensitivity analysis by varying the event water $\delta^{18}O$ values by $\pm 1.5‰$. The event water component was then further divided into an event surface-water component (Q_{es}) and an event subsurface-water component (Q_{ess}) by using changes in H_4SiO_4 concentrations in stream water as described previously. Temporal variations in H_4SiO_4 concentrations of event water are of less concern than those for $\delta^{18}O$ because melting snow contains so little H_4SiO_4 that plausible fluctuations have essentially no effect on the results.

The $\delta^{18}O$ data were used to divide the runoff from the rain event of March 17 into three components: (1) a pre-event water component, (2) an event snowmelt component, and (3) an event rainfall component. These components were distinguishable because the $\delta^{18}O$ of snowmelt (−17.98‰) differed significantly from the $\delta^{18}O$ of the rainfall (−11.75‰). In this separation, the event rainfall component was assumed to reduce the contribution of the other components by an amount equal to the proportions of the other two components that were present in the stream just before the rain began.

The separation of flow into event and pre-event water components through $\delta^{18}O$ analyses indicated that pre-event water was predominant in both streams throughout the March 13–16 melt period (Fig. 6); it constituted 80% of total streamflow at WO2, and 77% at WO4, and an increasing proportion of event water

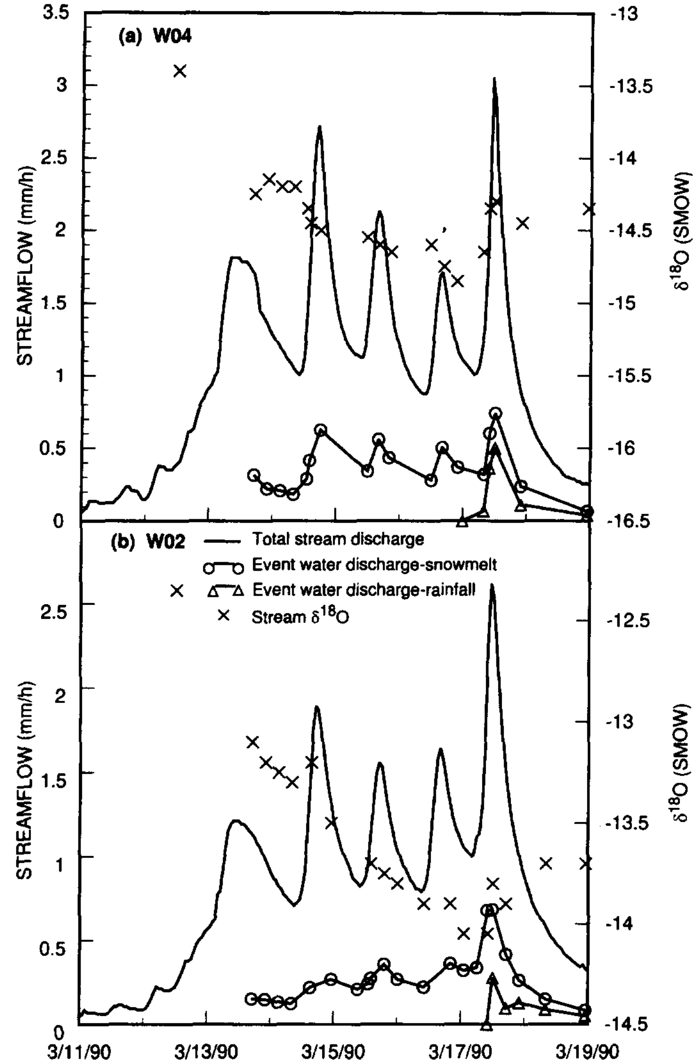

Fig. 6. Total stream discharge, event-water discharge, event-water discharge from rainfall on March 17, and $\delta^{18}O$ of stream water during the snowmelt of March 1990: (a) stream WO4; (b) stream WO2.

in each stream during each day of melting was evident. The greatest differences in event water proportions between the two streams occurred early in the melt period and narrowed through time. For example, event water constituted about 13% of streamflow in WO2 and 19% in WO4 at 5 p.m. on March 13, and 15% of streamflow in WO2, and about 23% in WO4 on March 14 in the late afternoon. By the peak of flow on March 15, the difference had narrowed—event water formed 25% of streamflow in WO2 and 26% in WO4. This pattern continued until March 17, when event water from the rainfall began to enter the streams. The peak flow on March 17 consisted of 62% pre-event water, 27% event snowmelt, and 11% event rain water in WO2, and 56% pre-event water, 26% event snowmelt, and 18% event rain water in WO4. Thus, even after 5 days of high flow in these streams, more than 50% of streamflow consisted of water that had resided in the catchment prior to March 13. These results demonstrate (1) the efficiency of mixing processes in the Woods Lake catchment, and (2) that pre-event storage in both

Table 2
Sensitivity analysis of source-water separations[a] during the March 1990 snowmelt. Percent event water is shown for the sample collected nearest the time of peak flow each day

Date	Time	$\delta^{18}O$ of snowmelt at WO2			$\delta^{18}O$ of snowmelt at WO4		
		Mean −17.98‰	Min. − 19.48‰	Max. −16.48‰	Mean −17.98‰	Min. − 19.48‰	Max. −16.48‰
3–13	5:00 p.m.	13	10	18	19	14	28
3–14	3:20 p.m.	15	12	21	23	17	34
3–15	7:00 p.m.	25	20	34	27	20	40
3–16	8:00 p.m.	28	22	38	32	24	47
All 4 dates		20	16	27	23	17	34

catchments exceeded snowmelt plus rainfall through the melt period. The sensitivity analysis demonstrated that the flow separations are not greatly affected by plausible temporal variations in $\delta^{18}O$ values of the melting snow that may have gone undetected by the sample collection schedule during the melt period (Table 2). The pre-event component remained predominant throughout the melt period at both streams. The separations for WO4 were more sensitive to variations in snowmelt $\delta^{18}O$ than the separations for WO2 because the $\delta^{18}O$ difference between pre-event water and event water at WO4 was less than at WO2. For example, the range in the event water component on March 16 at 8 p.m. in WO2 was from 22 to 38%, whereas the range for WO4 at the same time was from 24 to 47%.

The separation of event water into surface-water and subsurface-water components on the basis of H_4SiO_4 concentrations indicated that, in general, the subsurface component was greater than the surface component throughout the March 13–16 melt period in both streams (Table 3), but the surface-water component dominated in both streams during the rain-on-snow event of March 17. Surface water formed about 68% of the event water component at WO2 and 75% at WO4 near the time of peak flow on March 17, but the percentage declined rapidly after the rain ceased. In general, the event water component contained a greater proportion of surface water at WO4 than at WO2. Cirmo and Driscoll (1996) discuss the possibility of enhanced silica mobilization from the sediments of the beaver pond in WO2 after liming, and attribute the response to dissolution of diatom frustules under elevated pH and DOC concentrations. Their explanation could in part, be responsible for the apparent lower proportion of event surface water in peak flow at WO2.

4.3.2. Spring rain event (May 1990)

Samples for $\delta^{18}O$ analysis were collected during a 51 mm spring rainstorm on May 16–18, 1990 (Fig. 7). The rainfall was divided into three distinct periods: (1) rain of low intensity from 2 p.m. on May 16 to 12 p.m. on May 17 (10 mm), (2) rain of moderate intensity from 12 p.m. to 3 p.m. on May 17 (31 mm), and (3) occasional rain of low intensity from 3 p.m. on May 17 through the end of May 18 (10 mm). Stream discharge on May 16 just prior to the onset of rain was 0.08 mm h^{-1} at WO4 and 0.14 mm h^{-1} at WO2 indicating relatively dry antecedent conditions. Stream discharge peaked on May 17 at 6 p.m. at WO4 and at 10 p.m. at WO2, and continued to decline through May 18 despite continued occasional light rain. The storm produced 31 mm of runoff at WO2 and 40 mm of runoff at WO4 through May 18. Runoff was 61% of precipitation at WO2 and 78% at WO4, significantly lower than for the March snowmelt period, but similar relative to each other with a greater runoff percentage at WO4 than at WO2.

The $\delta^{18}O$ of a bulk precipitation sample was −8.35‰, compared to −13.70 and −12.70‰ for pre-event base-flow samples from WO4 and WO2, respectively. The hydrograph separation for WO4 indicates an increasing proportion of event water as streamflow increased, reaching a maximum of 26% at peak flow on May 17 (Fig. 7). The proportion of event water at WO2 in contrast, ranged from 0 to 5% throughout the period. The low event water proportions in WO2 suggest that the beaver pond was able to retain nearly all event water during the storm. A

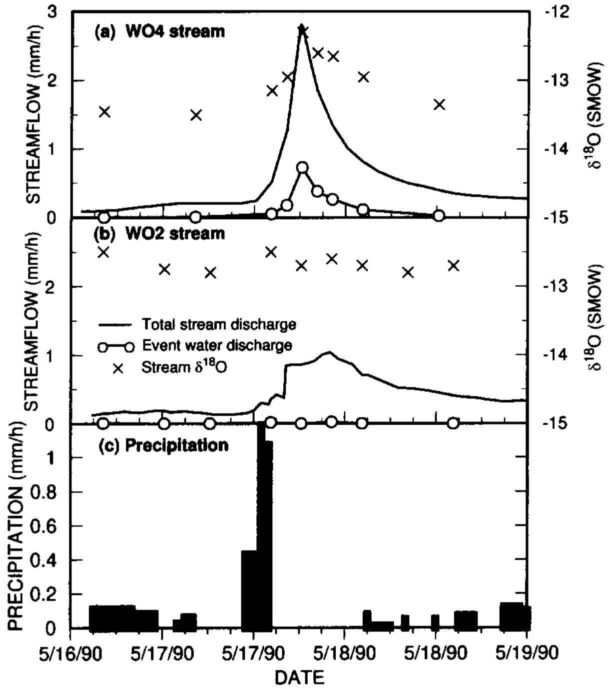

Fig. 7. Total stream discharge, event-water discharge, and $\delta^{18}O$ of stream water during the rain event of May 1990: (a) stream WO4; (b) stream WO2; (c) hourly precipitation.

separation of the event water component into surface water and subsurface water could not be attempted because streamflow H_4SiO_4 data were not available.

4.3.3. Autumn rain events

A limited number of samples were collected for $\delta^{18}O$ analysis from rain events during the fall of 1990, most were pre-event samples and peak-flow samples. These data are shown in Table 4, along with data from a rain storm during the fall of 1989. Most of the sampling was done in WO4, and samples were never successfully collected from both streams during the same rain event. October 1990, when most of the samples were collected, was a wet month in the region, with 167 mm of rain at Woods Lake, but the $\delta^{18}O$ data show that, even under wet antecedent conditions such as those in late October, stormflow consisted mostly of pre-event water. The proportion of event water at peak flow in WO4 was generally inversely related to the antecedent moisture conditions as estimated from base-flow discharge, and not to total event precipitation (Table 4). The hydrograph separation from the May 1990 storm whose antecedent moisture conditions were similar to those of the September 23, 1989 and October 4, 1990 storms is also broadly consistent with the observation that antecedent moisture conditions largely determine the proportions of source-water components. Rainfall intensity can also affect the relative proportions of source water components that are measured in the streams at peak flow. The September 23, 1989 and October 4, 1990 storms had similar pre-storm base flow and total precipitation, yet the peak-flow event water component was 39% for the fall 1989 event and only 22% for the fall 1990 event consistent with the significantly greater maximum hourly rainfall intensity for the 1989 storm (Table 4).

Separation of the event water component into surface and subsurface water on the basis of stream H_4SiO_4 concentrations indicates that almost no event surface water entered the streams during any of the autumn storms. Event surface water ranged from 0 to 2% of streamflow at peak flow in both streams for all of the storms that were sampled.

Table 3

The percent event surface water (Q_{es}), event subsurface water (Q_{ess}), and H_4SiO_4 concentrations in streamflow before the onset of significant snowmelt, and near the time of peak flow during March 12–17, 1990

Sampling date and time		H_4SiO_4 concentration (μmol l^{-1})		Event surface water (Q_{es})		Event subsurface water (Q_{ess})	
		WO2	WO4	WO2	WO4	WO2	WO4
March 12	12:00 p.m.	114.6	103.8	0	0	0	0
March 13	5:00 p.m.	106.4	96.6	7	7	6	12
March 14	6:00 p.m.	111.4	91.9	3	12	16	12
March 15	7:00 p.m.	107.4	87.2	6	16	19	11
March 16	8:00 p.m.	105.4	92.5	8	11	20	20
March 17	12:00 p.m.	85	69.8	26	33	12	11
March 17	5:00 p.m.	93	93.4	19	10	16	32

5. Discussion

5.1. Evaporation and short catchment residence times

Summer evaporation from the beaver pond had a measurable effect on stream runoff patterns at WO2, as shown by the summer change in the meteoric water line slope which was not evident in the line for WO4 (Fig. 3(c)). One of the effects of evaporation at WO2 would have been increased concentration of solutes in WO2 relative to WO4. The mean catchment residence times at base flow in WO2 and WO4 were not significantly different, however, or the difference was too small to be detected by the method used in this study (Table 1). These results suggest that the mean retention time of waters in the beaver pond is small relative to other retention processes in these catchments. Furthermore, the mean catchment residence times of about 100 days are short, consistent with the chronically acidic conditions at Woods Lake prior to calcium carbonate treatment.

5.2. Effects of the beaver pond at high flow

Differences in runoff characteristics between the two catchments were more significant at high flow than at base flow, and these differences were dependent on the season. The beaver pond in catchment WO2 acts as a reservoir in which water can be both mixed and stored. During the snowmelt period, peak flow in WO2 contained less event water than in WO4 for the first two days of the melt, but by the third day, the runoff components of the two streams differed little—a pattern that continued through the rest of the melt period (Fig. 6). This similarity in runoff response can be attributed to the lack of significant mixing in the pond during snowmelt (the pond was thermally stratified in winter; Cirmo and Driscoll, 1996); a similar snowmelt runoff response has been observed in Woods Lake itself, where thermal stratification prevents mixing of snowmelt runoff below a depth of 1–1.5 m in the lake, allowing the rapid transport of inlet stream water to the lake outlet (Gubala

Table 4

Hydrological data and percent event water in samples collected at peak flow during autumn rain events

Stream	Date	Rainfall (mm)	Runoff/precip. (%)	Max. precip. intensity (mm h^{-1})	Pre-event base flow (mm h^{-1})	Event water (%)
WO4	9–23–89	30	70	14	0.11	39
WO4	10–4–90	29	45	5	0.075	22
WO4	10–9–90	25	76	2	0.15	17
WO4	10–23–90	39	97	10	0.35	15
WO2	10–18–90	43	65	11	0.19	16

et al., 1991). Even if the meltwater had completely mixed within the pond, streamflow was great enough to decrease the residence time within the pond to about 24 h on March 14–16, and about 17 h on March 17 (assuming complete mixing, and a pond volume of 7500 m^3, reported in Cirmo and Driscoll, 1996). Such a short retention time probably was not a significant factor relative to retention and mixing processes that were occurring in catchment soils and in the till at this time.

In contrast to the March snowmelt, nearly all the event water at WO2 was retained in the beaver pond during the rain event later in the spring (May 1990), whereas event water represented 26% of peak flow at WO4 (Fig. 7). By May, the beaver pond level was lower and the temperature of the runoff was similar to that of pond water, both of which would tend to increase storage and mixing in the pond. Additionally, the total amount of precipitation for the May rain event (51 mm) was significantly less than for the March snowmelt (186 mm). The runoff response (95–100% pre-event water) measured in WO2 during the May rain event is probably a common occurrence in this catchment during the ice-free season, depending on the antecedent pond level, degree of stratification in pond waters, and the amount and intensity of precipitation. The runoff response of WO2 to the rainfall of October 18, 1990 shows, however, that a significant proportion of the runoff (about 16%) was event water. This rainfall occurred during a wet month, however, when the level of the beaver pond was probably quite high, minimizing the ability of the pond to store runoff.

5.3. Importance of subsurface flow

The results of this study indicate that pre-event water is the largest component of high flow in these two lake tributary streams, and that subsurface stormflow is the dominant event water flowpath during storms. For example, the sum of the pre-event water and event subsurface water components for the March snowmelt indicates that about 80% of stream peak flow came from subsurface flow, except for at the peak of the March 17 rain-on-snow event. Similarly, subsurface flow accounted for more than 95% of peak streamflow during the autumn rain events. These results are similar to those reported by Wels et al. (1991) for small catchments on the Canadian Shield.

5.4. Comparison to other wetlands-influenced catchments

Mixing of pre-event water with event water in permanently saturated areas was found to control runoff processes in a small catchment containing wetlands near Toronto, Canada (Hill and Waddington, 1993). If this process is important to the stormflow response in these Adirondack catchments, then WO2 (with saturated areas surrounding the beaver pond) should have had a greater proportion of event water at high flow than WO4 (with no permanent wetlands)—but just the opposite was found (Table 3). The WO2 catchment differs from the wetland catchment that Hill and Waddington (1993) studied, in that much of the original wetland in the WO2 catchment is now occupied by a beaver pond. Discharge from that pond, which drains 98% of the WO2 catchment, is regulated by the beaver dam. Under high-flow conditions, water can spill over the top of the dam, but under dry conditions, most flow occurs through the dam itself. The hydrograph separations for the storm of May 1990 show that the pond can effectively contain all the event water for a moderate storm (51 mm) under dry antecedent conditions, whereas the nearby stream (WO4) with no beaver pond was 26% event water at peak flow (Fig. 7). This effective retention by the pond of an amount of precipitation nearly double the estimated capacity of the pond (26 mm), suggests that the adjacent wetlands can retain a large amount of stormflow under dry antecedent conditions.

6. Conclusions and implications for catchment liming

Results of this study show that mixing and retention in a beaver pond affects some but not all, aspects of catchment hydrology. The residence times of base flow in the WO2 and WO4 catchments were similar at about 100 days, although evaporation from the beaver pond affected the slope of the meteoric water line and caused the $\delta^{18}O$ values of WO2 to be significantly greater in the summer and fall than those in WO4. Pre-event water was the predominant component of high flow runoff in both streams, and most event water generally passed through the subsurface prior to entering the stream channel. The effect of the beaver pond on high-flow source-water components was a function of the water temperature, precipitation amount, antecedent moisture conditions, and pre-event pond storage. The interaction of these variables produced either little difference between WO2 and WO4 in source-water components (latter part of March snowmelt), or a large difference in the same runoff components (May rain event). These results are important because an increasing beaver population in North America (Naiman et al., 1988) has resulted in the flooding and impoundment of an increasing number of wetlands in upland catchments. Beaver ponds have previously been shown to strongly affect the biogeochemical cycling of nitrogen, sulfur, carbon, and redox-sensitive metals in the Adirondack region (Cirmo and Driscoll, 1993, 1996; Burns, 1996). Thus, beaver ponds are likely to affect runoff from an increasing number of catchments and, therefore, warrant further study.

The impoundment retained nearly all the event water during rain storms such as that of May 1990. Therefore, in the absence of calcium carbonate treatment, such impounded catchments would retain most of the acidic runoff that causes short-term declines in pH and alkalinity in this region (Wigington et al., 1996). The event water that does not escape the pond could then potentially be neutralized by the reduction processes that commonly occur in beaver ponds (Cirmo and Driscoll, 1993). The addition of calcium carbonate to the sediment of a beaver pond (such as at Woods Lake) would further enhance this neutralizing effect (Cirmo and Driscoll, 1996). The conclusion that most event water passes through the subsurface before entering the stream during events is consistent with the episodic stream chemistry response that indicates partial neutralization of storm runoff by H^+–Ca^{2+} exchange in the soil (Newton et al., 1996).

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References

Abdul, A.S., Gillham, R.W., 1989. Field studies of the effects of the capillary fringe on streamflow generation, J. Hydrol., 112, 1–18.

April, R., Newton, R.M., 1985. Influence of geology on lake acidification in the ILWAS catchments, Water Air Soil Pollut., 26, 373–386.

Bonell, M., 1993. Progress in the understanding of runoff generation dynamics in forests, J. Hydrol., 150, 217–275.

Brown, V.A., McDonnell, J.J., Burns D.A., Kendall, C., 1997. The role of event water, rapid shallow flowpaths, and catchment size in summer stormflow at an upland watershed in the Catskill Mountains of New York. J. Hydrol. (under review).

Burns, D.A., 1996. The effects of liming an Adirondack lake catchment on downstream water chemistry, Biogeochemistry, 32, 197–220.

Buttle, J.M., 1994. Isotope hydrograph separations and rapid delivery of pre-event water from drainage basins, Prog. Phys. Geogr., 18, 16–41.

Cirmo, C.P., Driscoll, C.T., 1993. Beaver pond biogeochemistry: acid neutralizing capacity generation in a headwater stream, Wetlands, 13, 277–292.

Cirmo, C.P., Driscoll, C.T., 1996. The impacts of a catchment $CaCO_3$ treatment on stream and wetland biogeochemistry in the Adirondack Mountains, Biogeochemistry, 32, 123–156.

Coplen, T.B., 1988. Normalization of oxygen and hydrogen isotope data, Chem. Geol., 72, 293–297.

Cronan, C.S., 1985. Biogeochemical influence of vegetation and soils in the ILWAS catchment, Water Air Soil Pollut., 26, 355–371.

DeWalle, D.R., Swistock, B.R., Sharpe, W.E., 1988. Three-componentracer model for stormflow on a small Appalachian forested catchment, J. Hydrol., 104, 301–310.

Dincer, T., Payne, B.R., Florkowski, T., Martinec, J., Tongiorgi, E., 1970. Snowmelt runoff from measurements of tritium and oxygen-18, Water Resour. Res., 6, 110–124.

Driscoll, C.T., Cirmo, C.P., Fahey, T.J., Blette, V.L., Bukaveckas, P.A., Burns, D.A., Gubala, C.P., Leopold, D.J., Newton, R.M., Raynal, D.J., Schofield, C.J., Yavitt, J.B., Porcella, D.B., 1996. The experimental catchment liming study: comparison of lake and catchment neutralization strategies, Biogeochemistry, 32, 1–32.

Eriksson, E., 1958. The possible use of tritium for estimating groundwater storage, Tellus, 10, 472–478.

Geary, R.J., Driscoll, C.T., 1996. Forest soil solutions: acid/base chemistry and response to calcite treatment, Biogeochemistry, 32, 53–78.

Goldstein, R.A., Chen, C.W., Gherini, S.A., 1985. Integrated lake-catchment acidification study: summary, Water Air Soil Pollut., 26, 327–337.

Gubala, C.P., Driscoll, C.T., Newton, R.M., Schofield, C.L., 1991. Chemistry of a near-shore lake region during spring snowmelt, Environ. Sci. Technol., 25, 2024–2030.

Harris, D.M., McDonnell, J.J., Rodhe, A., 1995. Hydrograph separation using continuous open system isotope mixing, Water Resour. Res., 31, 157–171.

Hill, A.R., Waddington, J.M., 1993. Analysis of storm run-off sources using oxygen-18 in a headwater swamp, Hydrol. Proc., 7, 305–316.

Hursh, C.R., Brater, E.F., 1941. Separating storm-hydrographs from small drainage areas into surface- and subsurface-flow, Trans. Am. Geophys. Union, 22, 863–870.

International Atomic Energy Agency, 1981. Statistical treatment of environmental isotope data in precipitation. Technical Report Series No. 206, IAEA, Vienna, Austria, 255 pp.

International Atomic Energy Agency, 1983. Isotope techniques in the hydrogeological assessment of potential sites for the disposal of high-level radioactive wastes. Technical Report Series No. 228, IAEA, Vienna, Austria, 151 pp.

Johnston, C.A., Naiman, R.J., 1987. Boundary dynamics at the aquatic–terrestrial interface: the influence of beaver and geomorphology, Landscape Ecol., 1, 47–57.

Kendall, C., Sklash, M.G., Bullen, T.D., 1995. Isotope tracers of water and solute sources in catchments. In: S.T. Trudgill (Ed.), Solute Modeling in Catchment Systems. Wiley, London, pp. 261–303.

Kennedy, V.C., 1971. Silica variation in stream water with time and discharge. In: J.D. Hem (Editor), Non-equilibrium Systems in Natural Water Chemistry, Adv. Chem. Ser. 106. American Chemical Society, Washington, DC, pp. 106–130.

McDonnell, J.J., 1990. A rationale for pre-event water discharge through macropores in a steep, humid catchment, Water Resour. Res., 26, 2821–2832.

Maloszewski, P., Rauert, W., Stichler, W., Herrmann, A., 1983. Application of flow models in an alpine catchment area, J. Hydrol., 66, 319–330.

Martinec, J., Siegenthaler, U., Oeschger, H., Tongiorgi, E., 1974. Event insights into the run-off mechanism by environmental isotopes. In: Isotope Techniques in Groundwater Hydrology. International Atomic Energy Agency, Vienna, Austria, pp. 129–143.

Maulé, C.P., Stein, J., 1990. Hydrologic flow path definition and partitioning of spring meltwater, Water Resour. Res., 26, 2959–2970.

Mulholland, P.J., 1993. Hydrometric and stream chemistry evidence of three storm flowpaths in Walker Branch catchment, J. Hydrol., 151, 291–316.

Naiman, R.J., Johnston, C.A., Kelley, J.C., 1988. Alteration of North American streams by beaver, BioScience, 38, 753–762.

Naiman, R.J., Pinay, G., Johnston, C.A., Pastor, J., 1994. Beaver influences on the long-term biogeochemical characteristics of boreal forest drainage networks, Ecology, 75, 905–921.

Newton, R.M., Burns, D.A., Blette, V.L., Driscoll, C.T., 1996. Effect of whole catchment liming on the episodic acidification of two Adirondack streams, Biogeochemistry, 32, 157–180.

Ogunkoya, O.O., Jenkins, A., 1993. Analysis of storm hydrograph and flow pathways using a three-component hydrograph separation model, J. Hydrol., 142, 71–88.

Peters, N.E., Murdoch, P.S., 1985. Hydrogeologic comparison of an acidic-lake basin with a neutral-lake basin in the west-central Adirondack Mountains, New York, Water Air Soil Pollut., 26, 387–402.

Pinder, G.F., Jones, J.F., 1969. Determination of the groundwater component of peak discharge from the chemistry of total run-off, Water Resour. Res., 5, 428–445.

Porcella, D.B., 1989. Lake acidification mitigation project (LAMP): an overview of an ecosystem perturbation experiment, Can. J. Fish. Aquat. Sci., 46, 246–248.

Sklash, M.G., 1990. Environmental isotope studies of storm and snowmelt runoff generation. In: M.G. Anderson, T.P. Burt (Eds.), Process Studies in Hillslope Hydrology. John Wiley, London, pp. 401–435.

Sklash, M.G., Farvolden, R.N., Fritz, P., 1976. A conceptual model of catchment response to rainfall, developed through the use of oxygen-18 as a natural tracer, Can. J. Earth Sci., 13, 271–283.

Stewart, M.K., McDonnell, J.J., 1991. Modeling base flow soil water residence times from deuterium concentrations, Water Resour. Res., 27, 2681–2693.

Stichler, W., 1987. Snowcover and snowmelt processes studied by means of environmental isotopes. In: H.G. Jones, W.J. Orville-Thomas (Eds.), Seasonal Snowcovers: Physics, Chemistry, Hydrology, NATO ASI Series, Series C: Mathematics and Physical Science, 211. D. Reidel, Hingham, MA, pp. 673–726.

Turner, J.V., Macpherson, D.K., 1990. Mechanisms affecting streamflow and stream water quality: an approach via stable isotopes, hydrogeochemical, and time series analysis, Water Resour. Res., 26, 3005–3019.

Wels, C., Cornett, R.J., LaZerte, B.D., 1991. Hydrograph separation: a comparison of geochemical and isotopic tracers, J. Hydrol., 122, 253–274.

Wigington, P.J., DeWalle, D.R., Murdoch, P.S., Kretser, W.A., Simonin, H.A., Van Sickle, J., Baker, J.P., 1996. Episodic acidification of small streams in the northeastern United States: ionic controls of episodes, Ecol. Appl., 6, 389–407.

Woo, M.-K., Waddington, J.M., 1990. Effects of beaver dams on subarctic wetland hydrology, Arctic, 43, 223–230.