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Determination of hydrologic pathways during snowmelt for alpine/subalpine basins, Rocky Mountain National Park, Colorado

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Abstract. Alpine/subalpine ecosystems in Rocky Mountain National Park may be sensitive to atmospherically derived acidic deposition. Two- and three-component hydrograph separation analyses and correlation analyses were performed for six basins to provide insight into streamflow generation during snowmelt and to assess basin sensitivity to acidic deposition. Three-component hydrograph separation results for five basins showed that streamflow contained from 42 to 57% direct snowmelt runoff, 37 to 54% subsurface water, and 4 to 13% direct rain runoff for the May through October 1994 study period. Subsurface contributions were 89% of total flow for the sixth basin. The reliability of hydrograph separation model assumptions was explored. Subsurface flow was positively correlated with the amount of surficial material in a basin and was negatively correlated with basin slope. Basins with extensive surficial material and shallow slopes are less susceptible to ecosystem changes due to acidic deposition than basins with less surficial material and steeper slopes. This study was initiated to expand the intensive hydrologic research that has been conducted in Loch Vale basin to a more regional scale.

1. Overview

Hydrologic processes are governed by the permeability of, and flow paths through, surface and subsurface reservoirs. In alpine/subalpine basins, permeability generally is high and flow paths are short, so water has relatively little opportunity to react with soil and vegetation. Because of this, waters draining granitic terrains, such as Rocky Mountain National Park (RMNP), Colorado, typically are dilute, with median alkalinity <200 μeq/L and specific conductance <50 μS/cm [*Eilers et al.*, 1987; *Landers et al.*, 1987; *Turk and Spahr*, 1991]. High permeability, short flow paths, and shallow soils also limit the ability of biota to consume atmospherically deposited nitrogen [*Baron and Campbell*, 1997; *Campbell et al.*, this issue]. If the biota of a basin is unable to consume all of the deposited atmospheric nitrogen, nitrogen saturation may occur, causing surface water acidification and ecosystem changes [*Baron and Campbell*, 1997; *Baron et al.*, 1994; *Campbell et al.*, this issue; *Durka et al.*, 1994]. Atmospheric deposition of nitrogen to the Colorado Rocky Mountains has increased since the late 1970s [*Lynch et al.*, 1995], so nitrogen saturation is a possibility, with resultant detriment to the alpine/subalpine ecosystems. This study begins to assess the vulnerability of alpine/subalpine basins in RMNP to potential acidification by exploring the routing of snowmelt water through six basins.

Hydrologic processes have an important bearing on the acidity of surface waters [*Shanley and Peters*, 1988]. Substantial variability can exist in hydrologic processes and surface water chemistry within and among alpine/subalpine basins because of differences in residence times of, and materials encountered by, water following diverse flow paths. Researchers have employed hydrograph separation techniques using a mass balance of naturally occurring tracers to estimate the flow of water through various hydrologic pathways. Hydrograph separation mass balance models rely on the assumption that tracer concentrations of various sources of water, such as groundwater, soil water, snowmelt, or rainfall, are different enough to distinguish these sources.

The definition of streamflow sources, or components, depends on the tracer used. Chemical tracers such as sodium and silica provide information on the geochemical reactions that are associated with flow paths of water [*Caine*, 1989b; *Eshleman et al.*, 1995; *Hooper and Shoemaker*, 1986]. For example, precipitation water that reaches a stream without interacting with soil or bedrock may be considered "unreacted" with respect to geochemical processes such as ion exchange or mineral weathering, whereas infiltrated precipitation water that has acquired solutes while traveling along subsurface flow paths may be considered "reacted." Nonreactive isotopic tracers of water such as ^{2}H, ^{3}H, and ^{18}O will not change, with the exception of evaporation, regardless of the flow path taken. Isotopic tracers may be used to differentiate between sources of streamflow such as "preevent" groundwater and "event" precipitation water [*Bottomley et al.*, 1986; *Dincer et al.*, 1970; *Fritz et al.*, 1976].

On an annual basis, snowmelt is the main hydrologic event in alpine/subalpine basins. Snowmelt water typically is more acidic than resident subsurface water (soil water and groundwater) and may induce transient changes, such as a depression in pH, in stream water composition in small alpine basins [*Baron*, 1992; *Caine*, 1989a; *Tranter et al.*, 1987; *Williams and Melack*, 1991]. However, this response can be buffered by the displacement of subsurface water by infiltrating snowmelt or by snowmelt following a reactive pathway before discharging to the stream. Several studies in the Colorado Front Range have

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shown that while streamflow increased over 2 orders of magnitude during snowmelt, concentrations of most mineral weathering solutes varied by less than a factor of 3 [*Barry and Price*, 1987; *Campbell et al.*, 1995; *Mast et al.*, 1995]. This buffered response of mineral weathering solute concentrations to dilute snowmelt input suggests that much of the snowmelt may be routed through subsurface matrices, thus reacting with mineral surfaces before discharging to surface waters [*Caine*, 1989b; *Mast et al.*, 1995; *Sueker*, 1995].

Clow and Sueker [this issue] explored the interrelations of basin physical characteristics and stream water solute concentrations for nine alpine/subalpine basins in RMNP. In this study we explore the mechanisms of streamflow generation during snowmelt and the effects of basin physical characteristics on hydrologic processes for six of these collocated basins. By comparing multiple basins, we can begin to assess the extent of interbasin variability in streamflow generation and water chemistry. Hydrograph separation calculations were performed for the 1994 snowmelt period to explore the extent of subsurface routing of snowmelt through these basins, changes in contributions from different sources over time, and variability among basins. This study was initiated to expand the intensive hydrologic research that has been conducted in the Loch Vale basin to a more regional scale.

2. Methods

2.1. Site Descriptions

Stream discharge and chemistry data were collected in 1994 from six alpine/subalpine basins in Rocky Mountain National Park, located in the Front Range about 100 km northwest of Denver, Colorado (Figure 1). These steep-gradient basins reside on the eastern side of the Continental Divide and range in area from 780 to 10,440 ha (Table 1). Bedrock is composed of Precambrian biotitic gneiss and Silver Plume Granite, which have similar mineralogies [*Braddock and Cole*, 1990]. Soils are poorly developed [*Baron*, 1992] and decrease in thickness and maturity with increasing elevation [*Clow et al.*, 1997]. *Clow and Sueker* [this issue] provide detailed descriptions of the study area and the identifying physical characteristics of five environments found in these basins: tundra, bedrock, talus, subalpine meadow, and forest. Basin physical characteristics were quantified using digital topographic, vegetation, and geologic maps obtained from the National Park Service (Rocky Mountain National Park, unpublished data, 1996).

2.2. Field Procedures

Depth-integrated snow samples were collected for sodium and $\delta^{18}O$ analyses at peak snow accumulation in mid-April using an aluminum snow-coring device. Eight snow samples were collected from Boulder Brook basin (elevation range 2800–3100 m), and six were collected from Fern Creek basin (elevation range 2900–3060 m) (Table 2). Summer rainfall amount (including snow, hail, and graupel) and $\delta^{18}O$ content were measured for samples collected approximately weekly from May through October from five bulk rain gages placed near the basin outlets (elevation range 2500–2680 m) (Figure 1). Rain gages were fitted with looped polyethylene tubing to reduce evaporative losses. Additional isotopic data from rain samples collected in Loch Vale (elevation 3200 m) (Figure 1) were provided by A. Mast (U.S. Geological Survey, personal communication, 1994). The Loch Vale data were used with the data from the five bulk rain gages to develop an elevationally averaged rainfall isotopic composition based on basin area in successive 100-m elevation bands (Figure 2a) [*Sueker*, 1996]. Weekly precipitation amounts and sodium concentration data for rain and snow were obtained from two National Atmospheric Deposition Program (NADP) weather stations located in Rocky Mountain National Park (elevations of 2490 and 3159 m) (Figure 1) (NADP/National Trends Network (NTN), Annual data summary, Precipitation chemistry in the United States, NADP/NTN Coordination Office, Illinois State Water Survey, Urbana, 1984–1998, http://nadp.sws.uiuc.edu/) (hereinafter referred to as NADP/NTN, 1984–1998). Additional rainfall, snow depth, and snow water equivalence data were obtained from 10 Natural Resources Conservation Service snowpack telemetry (SNOTEL) stations (elevation range 2620–3260 m) (Figure 1) [*Soil Conservation Service*, 1994]. Rainfall data from the three sources were used to develop weekly total, elevationally averaged rainfall amounts (Figure 2a) [*Sueker*, 1996]. Total annual precipitation estimates for each basin were based on a chloride budget (Table 3) [*Sueker*, 1996]. Total elevationally averaged rainfall was subtracted from total annual precipitation to estimate total snowfall.

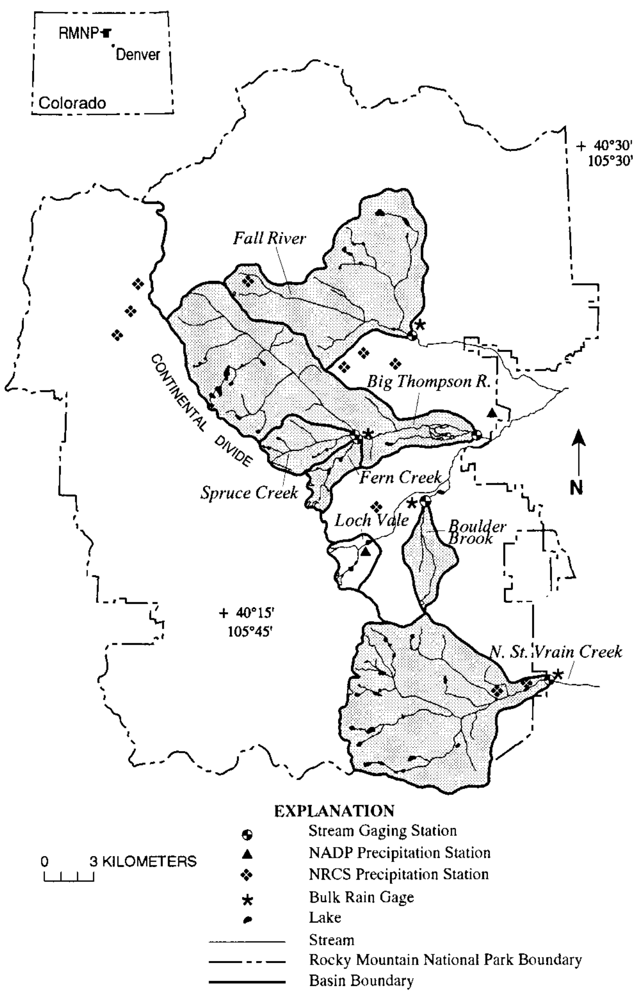

Figure 1. Location of study basins (shading) in Rocky Mountain National Park.

Current meter and dye-tracer discharge measurements were made periodically over a wide range of discharges during open-channel flow in 1993 and 1994 in Boulder Brook, Fern Creek,

Table 1. Characteristics of Study Basins in Rocky Mountain National Park, Colorado

	Fern Creek	Boulder Brook	Spruce Creek	Fall River	North St. Vrain Creek	Big Thompson River
General Site Information						
Area, ha	780	990	1,320	6,280	8,500	10,440
Elevation at gage, m	2,575	2,689	2,585	2,595	2,525	2,450
Maximum elevation, m	3,768	4,345	3,939	4,133	4,345	3,939
Median slope, deg	22	17	22	22	17	20
Basin area >30°, %	29	2	29	23	15	21
Cover Types From Geologic Map[a]						
Granite, %	7	31	34	43	34	47
Schist and gneiss, %	63	6	34	34	15	34
Young debris,[b] %	10	1	11	5	10	5
Old debris,[c] %	19	62	20	17	39	13
Cover Types From Aerial Photos[a]						
Tundra, %	16	34	30	28	18	23
Unvegetated, %	45	28	45	32	36	31
Forest, %	37	32	23	35	42	41
Subalpine meadow, %	2	6	2	5	4	5

[a]Data are obtained from Geographic Information System databases developed from U.S. Geological Survey topographic and geologic maps and National Park Service aerial photographs.
[b]Mapped areas of alluvium, colluvium, landslide deposits, and till are included.
[c]Mapped areas of talus and rock glacier are included.

and Spruce Creek (Figure 2b). Discharge rating curves (r^2 = 0.92 or greater), based on a minimum of 25 discharge measurements, were applied to stage data collected at 15-min intervals from float-type stage recorders mounted atop 10-cm stilling wells (Table 3) [*Sueker*, 1996]. Discharge data for North St. Vrain Creek were provided by the U.S. Geological Survey (USGS) [*Ugland et al.*, 1994], and discharge data for Fall River and Big Thompson River were provided by J. Hughes (National Park Service, personal communication, 1995) (Table 3 and Figure 2b).

Streamflow samples were collected approximately monthly from mid-January, early February, or March through mid-April, weekly from mid-April through August, and biweekly in September and October 1994 for sodium analysis (Figure 2c). Sample collection for δ^{18}O analysis began in March (Figure 2d). Samples were collected from the sites in the same order for each sampling event at about the same time of day for each site (±1 hour). Surface water and groundwater seep samples were collected from Boulder Brook (2927–3793 m) and Fern Creek (2591–3341 m) basins during summer synoptic sampling events (Table 2) [*Sueker*, 1996]. Average synoptic groundwater sodium concentrations for Fern Creek and Boulder Brook basins were compared with base flow values using the parametric t test.

2.3. Laboratory Analyses

Water samples for sodium analyses were collected in 250-mL high-density polyethylene bottles that had been soaked in deionized water and triple rinsed with sample water prior to collection. Samples were filtered through a 0.45-μm polycarbonate filter and acidified to pH 2 using concentrated, high-purity nitric acid. Sodium concentrations were determined by

Table 2. Mean Sodium and δ^{18}O Concentrations for 1994 Snow, Base Flow, and Groundwater Samples

Sample Type and Location	Number of Samples[a]	Sodium, μeq/L Mean	Sodium, μeq/L Standard Deviation	δ^{18}O, ‰ Mean	δ^{18}O, ‰ Standard Deviation
Snow samples	14	1.7	0.6	−20.43	0.57
Base flow stream samples					
Fern Creek	4	44.2	1.4	−16.84	0.13
Boulder Brook	5	83.6	1.8	−15.45	0.09
Spruce Creek	3	51	4.6	−16.55	0.01
Fall River	2	82.1	1.9	−17.02	0.01
North St. Vrain Creek	3	80.3	3.2	−17.17	0.04
Big Thompson River	3	82.2	4.7	−16.54	0.17
Seep and spring samples					
Fern Creek (July 6, 1994)	6	38.2	17.1	−17.88	0.47
Fern Creek (August 17, 1994)	5	41.4	14.1	−17.29	0.82
Fern Creek average	11	39.7	15.2	−17.61	0.69
Boulder Brook (July 20, 1994)	3	87.5	23.3	−12.26	2.07
Boulder Brook (August 30, 1994)	4	81.2	28.1	−11.57	1.35
Boulder Brook (October 9, 1994)	3	87.6	12.4	−11.63	1.05
Boulder Brook average	10	85	20.7	−11.79	1.38

[a]For each basin the number of base flow stream samples analyzed for δ^{18}O is 2.

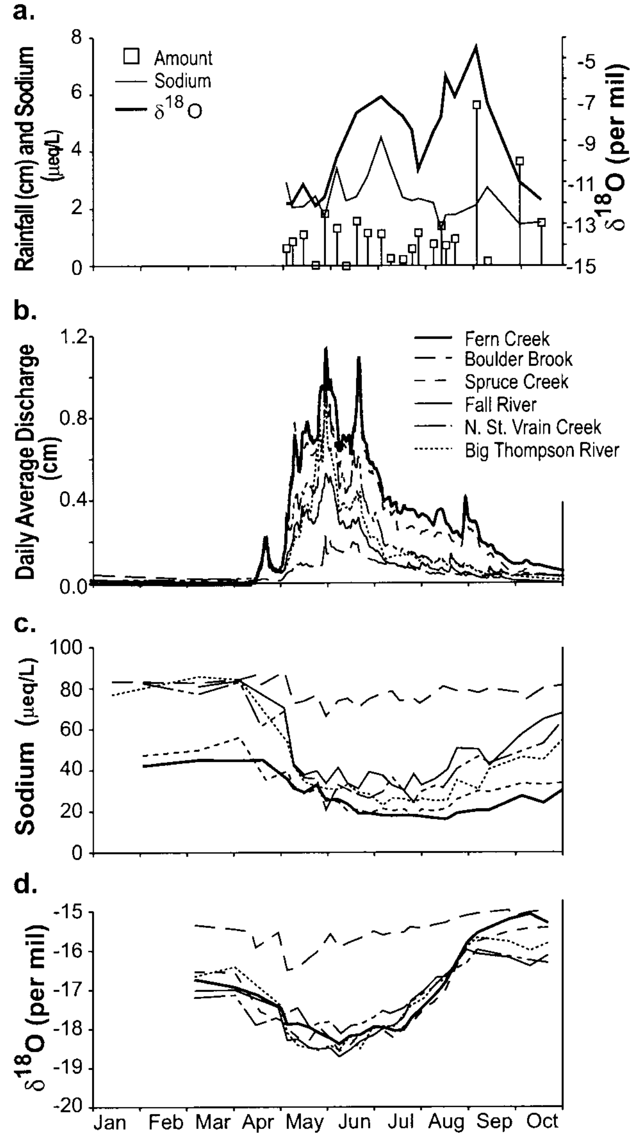

Figure 2. January through October 1994: (a) elevationally averaged rain amount, sodium concentration, and $\delta^{18}O$; (b) area-normalized daily average discharge; (c) stream water sodium concentrations; and (d) stream water $\delta^{18}O$ composition.

inductively coupled plasma atomic emission spectroscopy at the USGS Laboratory in Boulder, Colorado. The 1 σ precision was $\pm 5.4\%$, the accuracy of analysis based on replicate samples and reference standards was $\pm 5\%$, and the detection limit was 0.13 μeq/L. Isotope samples were collected in 15-mL borosilicate vials and capped with airtight caps. Analyses for $\delta^{18}O$ were performed at the USGS Isotope Laboratory in Menlo Park, California. The 1 σ precision was $\pm 0.05‰$, and accuracy of analysis based on replicate samples was $\pm 0.09‰$. Isotopic compositions are expressed as a δ(per mil) ratio of the sample to the Vienna standard mean ocean water standard, where R is the ratio $^{18}O/^{16}O$:

$$\delta^{18}O_{\text{sample}} = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 10^3. \qquad (1)$$

2.4. Hydrograph Separation Models

The isotopic and chemical responses of stream water to the input of snowmelt or rain depend on the sources, flow paths, and travel times of water as it moves from the point of input to the point of sampling [*Rodhe*, 1998]. Using sodium as a tracer in a two-component hydrograph separation model provides an estimate of the amount of precipitation water that reaches a stream without interacting with soils or acquiring mineral weathering products along the way. This water can be considered "unreacted" with respect to mineral weathering (Figure 3a). Soil water, groundwater, and infiltrated precipitation that have acquired mineral weathering products can be considered "reacted" with respect to mineral weathering.

Stable isotope data used in a two-component hydrograph separation describe the amount of event water and preevent water that reaches a stream (Figure 3b). In snowmelt-dominated systems the event is snowmelt, and event water refers to the input of water from melting of the snowpack. Preevent water refers to water that resided in the basin prior to snowmelt.

The reacted and unreacted components were estimated using [*Dincer et al.*, 1970]

$$Q_{\text{stream}} \times C_{\text{stream}} = Q_{\text{unreacted}} \times C_{\text{unreacted}} + Q_{\text{reacted}} \times C_{\text{reacted}}, \qquad (2)$$

with the mass balance constraint

$$Q_{\text{stream}} = Q_{\text{unreacted}} + Q_{\text{reacted}}, \qquad (3)$$

where Q is volume flow rate, C is sodium concentration, and the subscripts describe the water source. The event and preevent components were estimated by substituting $\delta^{18}O$ for sodium and substituting event and preevent for the unreacted and reacted components in the two-component model ((2) and (3)). Three conditions must be met for this two-component model: (1) The tracer composition of the event or unreacted component is significantly different from the tracer composition of the preevent or reacted component, respectively; (2) there are only two components contributing to streamflow; and (3) the tracer composition of each component is constant for the duration of the event or is known from measurements.

We adapted the three-component model developed by *Hinton et al.* [1994] to distinguish among contributions from snow, subsurface, and rain (Figure 3c). The mass balance for the three-component system is

$$C_{\text{stream}} \times Q_{\text{stream}} = C_{\text{subsurface}} \times Q_{\text{subsurface}} + C_{\text{snow}} \times Q_{\text{snow}} + C_{\text{rain}} \times Q_{\text{rain}}, \qquad (4)$$

with the constraint

$$Q_{\text{stream}} = Q_{\text{subsurface}} + Q_{\text{snow}} + Q_{\text{rain}}. \qquad (5)$$

When two tracers such as an isotopic and a chemical tracer are used, a set of linear equations can be solved for $Q_{\text{subsurface}}/Q_{\text{stream}}$, $Q_{\text{snow}}/Q_{\text{stream}}$, and $Q_{\text{rain}}/Q_{\text{stream}}$ [*Hinton et al.*, 1994].

Table 3. The 1994 Precipitation and Streamflow

Site	Rain	Snow	Total Precipitation	Total Streamflow
Fern Creek	23	84	108	71
Boulder Brook	24	31	55	22
Spruce Creek	24	51	74	55
Fall River	24	51	75	27
North St. Vrain Creek	24	76	99	45
Big Thompson River	24	51	75	35

Values are given in centimeters.

Four conditions must be satisfied for this three-component hydrograph separation model: (1) The tracer concentration of each component is distinct from the other two components for one or both of the tracers; (2) the tracer concentrations of the three components are not collinear; (3) only three components contribute to stream discharge; and (4) the tracer composition of each component is constant for the duration of the event or is known from measurements.

2.5. Tracer Concentrations for the Two- and Three-Component Models

Tracer concentrations for the reacted and preevent component in the two-component models were assumed to be equivalent to the mean measured base flow sodium and $\delta^{18}O$ values, respectively (Table 2). Mean base flow sodium and $\delta^{18}O$ values were also used for the subsurface component in the three-component model (Table 2). Measured streamflow values of sodium and $\delta^{18}O$ were used as inputs for stream tracer concentrations in the two- and three-component models (Figure 2). Weekly elevationally averaged rainfall amounts, sodium concentrations, and $\delta^{18}O$ composition were used for the rain component (Figure 2a). Enrichment of snowmelt runoff relative to bulk snowpack has been observed in previous studies [*Mast et al.*, 1995]. An event and snow component $\delta^{18}O$ value of −19.5‰ was chosen to account for this enrichment. A sodium concentration of 1.7 μeq/L was used for the unreacted and snow components (Table 2). Discharge was summed for each sampling period that was defined as beginning halfway in time between the current sample and the previous sample and ending halfway in time between the current sample and the next sample. Sample period results were summed to monthly values (Table 4). Model results were assumed to represent the amount of the pure end-member components represented in streamflow. Water in subsurface matrices is a mixture of rain and snow; therefore, component contributions of rain and snow are based on a short-timescale flow, rather than seasonal flow, of rain and snow water to the surface streams. The preevent, snow, and rain components are based on model assumption validations, and sensitivity analyses are presented in section 4.

3. Results

Elevationally averaged rainfall $\delta^{18}O$ for the summer of 1994 ranged from −4.5 to −12.1‰ and was lightest (most negative) in May and October when air temperatures were lowest (Figure 2a). The isotopic composition of rainfall varied by elevation during convective rainfall events (−0.04‰/100 m) but not during frontal storm events [*Sueker*, 1996]. Sodium concentrations in rain ranged from 1.3 to 4.5 μeq/L. The mean bulk snow sodium concentration and $\delta^{18}O$ content were 1.7 μeq/L and −20.43‰, respectively (Table 2). No correlation of elevation with sodium or $\delta^{18}O$ content in snow was noted. *Mast et al.* [1995] also found no correlation of elevation, snow depth, or snow water content with $\delta^{18}O$ in snow from 15 snow cores collected in Loch Vale in April 1994. Total precipitation in 1994 was 107% of the long-term average (1984–1998) for the Loch Vale NADP station and 91% of the long-term average (1980–1998) for the Beaver Meadow NADP station (NADP/NTN, 1984–1998). Estimated total precipitation for the basins ranged from 55 to 108 cm (Table 3).

In 1994 the lowest stream discharge occurred in late April, peak discharge occurred on June 1, and streamflow decreased toward base flow from July through October (Figure 2b). Low and peak flow discharges varied by a factor of 10^1 for Boulder Brook and $10^{1.9}$ for North St. Vrain Creek and varied between $10^{2.6}$ and $10^{3.0}$ for the remaining four streams. Discharge in May, June, and July accounted for 48–80% of total discharge for the year. A substantial increase in streamflow occurred in Fern and Spruce Creeks in early September in response to a rainfall event that produced approximately 6 cm of rain in a 2-week period (Figure 2). Boulder Brook maintained higher base flow and was much less responsive to snowmelt and rain relative to the other five basins. Total streamflow in 1994 ranged from 22.2 to 70.7 cm (Table 3).

Stream water sodium concentrations were highest during base flow (mid-January through early April) and were lowest during the July and August hydrograph recession period, with the exception of Boulder Brook, where the minimum concentration coincided with peak snowmelt (Figure 2c). Lowest and highest sodium concentrations differed by a factor of 1.3 for Boulder Brook and 2.8–4.0 for the other five streams. A seasonal change in the relation of discharge and stream concentrations of sodium was noted in all basins except Boulder Brook (Figure 4). Sodium concentrations in Fern Creek were higher at a specific stream discharge early in the melt period (May) than later in the melt period (July). The sodium concentration-discharge relation of the other streams closely resembled the relation in Fern Creek [*Sueker*, 1996]. Stream water $\delta^{18}O$ decreased from base flow values to a minimum

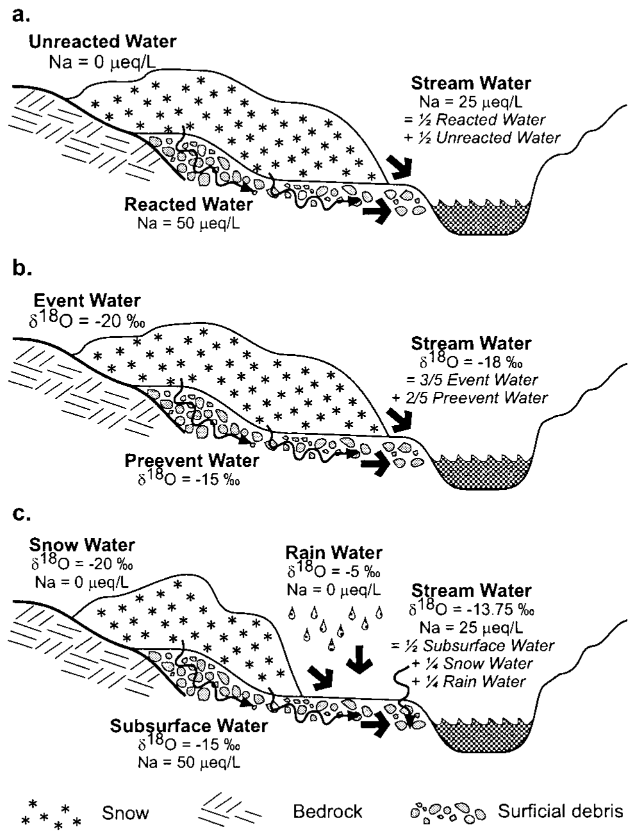

Figure 3. Schematic diagrams depicting information provided by hydrograph separations: (a) two-component model using a chemical tracer; (b) two-component model using an isotopic tracer; and (c) three-component model using dual chemical and isotopic tracers.

Table 4. Two- and Three-Component Hydrograph Separation Results for 1994

		Sodium		$\delta^{18}O$		Sodium and $\delta^{18}O$		
	Total Runoff, cm	Unreacted, %	Reacted, %	Event, %	Preevent, %	Snow, %	Rain, %	Subsurface, %
Fern Creek								
May	16.6	34	66	51	49	36	0	65
June	22.5	52	48	69	31	49	2	48
July	12.2	62	38	55	45	52	5	43
August	8.9	62	38	18	82	43	10	46
September	5	49	51	MF	MF	19	17	65
October	2.3	42	58	MF	MF	0	30	73
Total	67.5	50	50	53	47	42	5	54
Boulder Brook								
May	2.6	13	87	20	80	14	0	87
June	5	13	87	8	92	12	3	85
July	3	10	90	3	97	8	3	89
August	1.8	7	93	MF	MF	4	4	92
September	1.5	8	92	MF	MF	2	6	93
October	1.5	5	95	MF	MF	0	9	94
Total	15.4	11	89	10	90	8	4	89
Spruce Creek								
May	14	43	57	64	36	41	1	59
June	17.9	60	40	69	31	54	5	41
July	8.8	62	38	58	42	56	7	37
August	6.2	55	45	19	81	48	12	40
September	3.5	40	60	MF	MF	26	18	56
October	1.3	36	64	MF	MF	3	34	63
Total	51.7	53	47	58	42	47	7	47
Fall River								
May	7.9	53	47	67	33	48	3	50
June	9.6	56	44	76	24	56	2	42
July	3.3	59	41	46	54	54	7	39
August	2.3	50	50	MF	MF	40	15	45
September	1.1	37	63	MF	MF	26	17	57
October	0.5	20	80	MF	MF	9	17	74
Total	24.7	53	47	67	33	49	5	46
North St. Vrain Creek								
May	11.4	60	40	32	68	42	12	46
June	17	64	36	40	60	56	12	33
July	5.9	64	36	23	77	53	11	35
August	3.3	56	44	MF	MF	45	16	39
September	1.6	41	59	MF	MF	28	18	54
October	1.2	30	70	MF	MF	14	24	62
Total	40.4	60	40	33	67	49	13	39
Big Thompson River								
May	9.6	60	40	77	23	57	2	41
June	12.8	64	36	76	24	61	3	36
July	4.6	72	28	53	47	62	9	29
August	3.2	67	33	15	85	54	16	30
September	1.6	56	44	MF	MF	36	20	45
October	0.8	42	58	MF	MF	20	26	54
Total	32.6	63	37	67	33	57	6	37

MF indicates the model failed when $\delta^{18}O_{stream} > \delta^{18}O_{base\ flow}$.

during peak flow in May and June, then increased to maximum values in September or October (Figure 2d). Boulder Brook had the heaviest and least variable stream water $\delta^{18}O$ content.

Mean sodium concentrations of groundwater seep samples collected during 1994 synoptic sampling events were approximately 40 and 85 μeq/L for Fern Creek and Boulder Brook, respectively (Table 2). Mean base flow sodium concentrations for Boulder Brook and Fern Creek were not significantly different from mean concentrations in groundwater samples collected from the respective basins based on the parametric t test ($p < 0.05$). Thus base flow sodium concentrations represent average groundwater sodium concentrations for these two basins. This may not be true for the larger basins, where base flow contributions from lower-elevation, lower-gradient portions of the basins contain disproportionately high concentrations of mineral weathering products, compared to base flow contributions from higher-elevation, higher-gradient portions [*Sueker*, 1996].

Elevational transects of surface water samples collected from the Fern Creek basin in July and August 1994 show a progressive increase in streamflow sodium concentrations and ^{18}O content with decreasing elevation (Figure 5). Samples from the sites of highest elevation have the lowest sodium concentrations and plot in the lower left corner of the mixing diagram but are elevated above snow concentrations (Figure 5). The $\delta^{18}O$ of samples collected in July are depleted by about 1.3‰, and sodium concentrations are about 2 μeq/L less than samples collected in August.

Results of two-component hydrograph separation calculations ((2) and (3)) using sodium as a tracer show that most of the basins responded similarly to snowmelt runoff in 1994

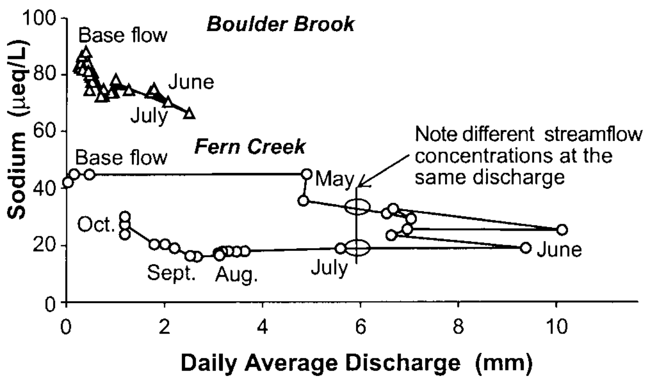

Figure 4. Concentration-discharge relations for Boulder Brook and Fern Creek 1994 stream flow. Concentration-discharge relations for Spruce Creek, Fall River, North St. Vrain Creek, and Big Thompson River are similar to Fern Creek.

(Table 4 and Figure 6). In response to snowmelt the contribution of unreacted water to streamflow increased rapidly in early May. Between early May and late August in the larger basins (Fall River, North St. Vrain Creek, and Big Thompson River), typically half or more of the total streamflow was provided by unreacted water. Contributions of unreacted water in Fern Creek and Spruce Creek did not reach 50% or more of streamflow until early to mid-June but declined at about the same time in late summer as the larger basins. In Boulder Brook the greatest contributions of unreacted water to streamflow occurred in May and June but reached a maximum of only 22%.

Results of two-component hydrograph separation calculations ((2) and (3)) using $\delta^{18}O$ as a tracer indicated that contributions of event water to streamflow varied greatly depending on the basin considered (Table 4 and Figure 6). During the May to October 1994 study period, event water accounted for 10% of total streamflow in Boulder Brook, 33% of total streamflow in North St. Vrain Creek, and 67% of total streamflow in Fall and Big Thompson Rivers (Table 4). Event-water contributions accounted for 53% and 58% of streamflow in Fern Creek and Spruce Creek, respectively.

Event-water contributions were highest from mid-May through June, corresponding to the period of maximum stream discharge, reaching 75% or more of total streamflow for all basins except North St. Vrain Creek and Boulder Brook (Figure 6). By midsummer the model predicted zero event-water contributions to streamflow. Owing to input of isotopically heavy (less negative) rain, streamflow values of $\delta^{18}O$ in middle to late summer exceeded the average of preevent values (Figure 2a), thus violating the model condition that only two sources contribute to streamflow. To address this problem, rainfall runoff was added as a third component in a three-component hydrograph separation model.

Most streamflow samples from early May through October 1994 plot within a mixing triangle for the basin and are well described as a mixture of the rain, snow, and subsurface components (Figure 7). Although not shown here, the mixing diagram for Spruce Creek is similar to the Fern Creek diagram, and mixing diagrams for North St. Vrain Creek and Fall River are similar to the Big Thompson River diagram [*Sueker*, 1996].

Results of the three-component hydrograph separations ((4) and (5)) using sodium and $\delta^{18}O$ as tracers indicate that the rain contribution typically was less than 5% of total streamflow in May and June, increased during late summer and fall, and reached a maximum in October (Table 4 and Figure 7). Although about 6 cm of rainfall occurred in the basins in August (Figure 2a), the rain component accounted for less than 1 cm of August streamflow (Table 4). Subsurface water provided 85–94% of total monthly streamflow in Boulder Brook and between 29 and 74% of total monthly streamflow for the other streams. Subsurface contributions were highest early in the snowmelt period and in September and October. Seasonal total snow contributions ranged from a low of 8% for Boulder Brook to 42–57% for the other five basins.

4. Discussion

The practice of using chemical and isotopic hydrograph separation techniques to trace the routing of water through basins started in the early 1970s [*Dincer et al.*, 1970; *Fritz et al.*, 1976; *Sklash et al.*, 1976; *Zeman and Slaymaker*, 1975]. The exact mechanisms governing the complex movement of water through a basin may not be discernible from hydrograph separation mass balance relations [*Dincer et al.*, 1970]; however, considerable insight is still gained by their use. Rain event studies [*Eshleman et al.*, 1993; *Fritz et al.*, 1976; *McDonnell et al.*, 1991; *Rodhe*, 1981] and snowmelt studies [*Bottomley et al.*, 1986; *Dincer et al.*, 1970; *Moore*, 1989; *Wels et al.*, 1990] in forested and low-altitude regions have shown that groundwater typically provides more than half of the total streamflow during periods of elevated runoff. Sufficient subsurface storage exists in these basins to strongly influence streamflow at all times of the year. *McNamara et al.* [1998] found that new water dominated streamflow during snowmelt in an arctic basin with permafrost; however, all summer storms were dominated by old water. They attributed the seasonal changes in old water contributions to increased subsurface storage capacity because of thawing of the active layer.

Chemical hydrograph separation results for small alpine basins (<200 ha) in the Rocky Mountains have shown that about half of the streamflow during the snowmelt period is return flow of melt waters that have passed through the subsurface matrix [*Caine*, 1989b; *Finley and Drever*, 1992; *Mast et al.*, 1995]. Streamflow response in the six study basins was varied, with return flow of both reacted water and subsurface water accounting for 37–89% of total streamflow for the 6-month study period (Table 4), although most streams were below 55%. Using the isotopic tracer $\delta^{18}O$, *Mast et al.* [1995] determined that preevent water contributed less than 20% of streamflow to

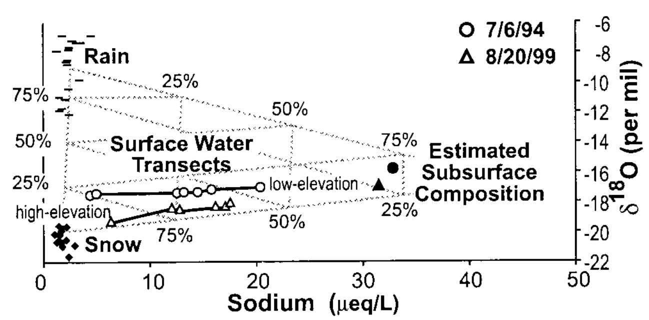

Figure 5. Elevational transects of sodium and $\delta^{18}O$ concentrations in surface water samples collected from Fern Creek basin. Open symbols are measured stream water compositions, and solid symbols are estimated subsurface compositions.

Andrews Creek, a 183-ha alpine subbasin of the Loch Vale basin, during snowmelt. Preevent contributions for the six study basins, all substantially larger in size, were much greater, accounting for 33–90% of streamflow.

4.1. Streamflow Mechanisms

The flow mechanisms described by *Williams et al.* [1993], *Mast et al.* [1995], and *Campbell et al.* [1995] for streamflow generation in alpine basins appear to be valid for most of the study basins and are supported by hydrograph separation results. The first fraction of meltwater infiltrates surficial deposits, including soils, talus, and till, displacing water that was residing in subsurface reservoirs before the snowmelt into the surface streams. Streamflow is dominated by the reacted, preevent, and subsurface components in this early part of the snowmelt period (Table 4 and Figures 6 and 7). Infiltrating snowmelt replaces the water in the subsurface reservoirs, undergoes rapid kinetic reactions with materials in the subsurface, and then is discharged to streamflow. However, the volume of snowmelt during peak flow can exceed the infiltration capacity of surficial deposits, and an increasing amount of snowmelt can find its way to streams via Hortonian overland flow [*Peters and Murdoch*, 1985; *Williams et al.*, 1993]. As the snowmelt season progresses, the reacted, preevent, and subsurface component contributions to streamflow are surpassed by unreacted, event, and snow component contributions, respectively. Evidence of an overland flow mechanism is shown in the difference between the unreacted and event components during peak flow. During the hydrograph recession, much of the streamflow is supplied by return flow of snowmelt from soils as contributions to streamflow from the unreacted and snow components decrease during this time. Rainfall runoff and recharge of soils becomes more important as the quantity of water available from snowmelt decreases. Rain component contributions to streamflow increase during the hydrograph recession, supplying about one quarter to one third of total streamflow by October.

Flow-duration curves provide additional insight into the processes that control streamflow. Steeply sloped flow-duration curves indicate control of hydrologic systems by surface runoff, while flatter slopes indicate control by groundwater discharge or surface storage, which delay flow from a basin [*Peters and Murdoch*, 1985]. The Boulder Brook flow-duration curve is much flatter than the curves for the other basins (Figure 8). Because surface water storage is minimal in this basin, the shallow curve demonstrates a groundwater discharge control on streamflow. This conclusion is supported by the very high reacted, preevent, and subsurface component contributions to streamflow estimated for this basin. During high flows the North St. Vrain Creek flow-duration curve resembles the curves of four of the other streams but is similar to the Boulder Brook curve beyond about the 60% exceedance level. As for most of the streams, unreacted and snow component contributions dominate streamflow in North St. Vrain Creek during snowmelt. However, there is sufficient storage in this basin,

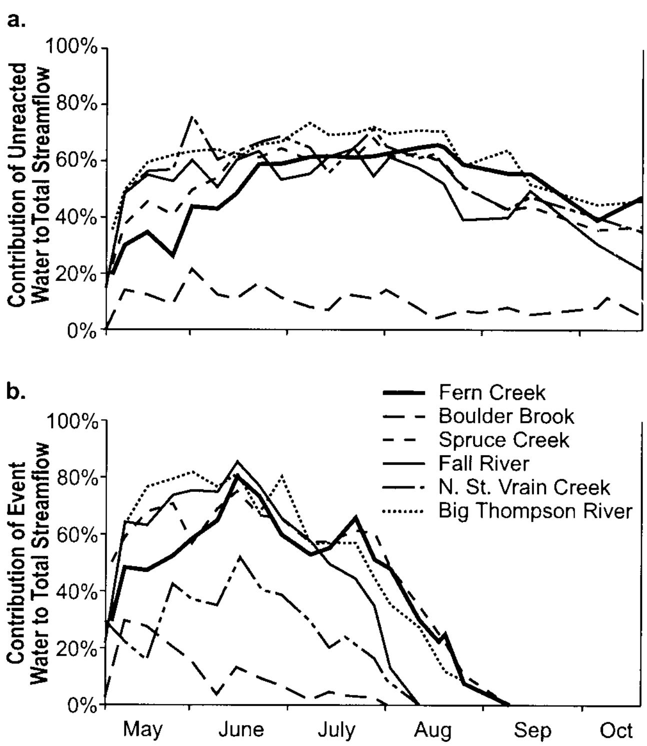

Figure 6. Results of two-component hydrograph separations using (a) sodium and (b) $\delta^{18}O$ as tracers.

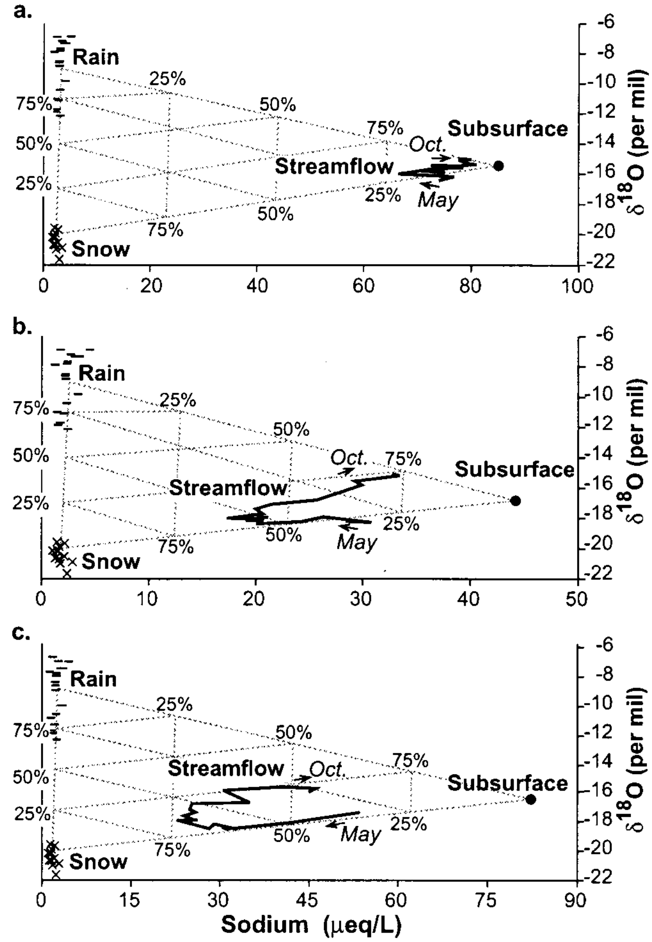

Figure 7. Three-component mixing diagram using sodium and $\delta^{18}O$ as tracers: (a) Boulder Brook, (b) Fern Creek, and (c) Big Thompson River. Results for Spruce Creek were similar to results for Fern Creek. Results for Fall River and North St. Vrain Creek were similar to results for Big Thompson River.

either in subsurface reservoirs or in the numerous lakes scattered throughout the basin, to cause a flatter flow-duration curve during lower-flow periods.

Water flowing through subsurface matrices has a longer residence time than water that follows a surface flow path. Estimates of sulfate ages, based on the activity of ^{35}S in sulfate, can be used to age date water, assuming conservative behavior of sulfate in the hydrologic system [*Michel and Turk*, 1995]. Water exiting Boulder Brook basin in early August and late October 1994 was approximately 200 days older than water exiting Fern and Spruce Creek basins [*Sueker et al.*, 1999]. Age differences were attributed to geomorphic differences between the basins (Table 1); that is, extensive surficial debris and shallow slopes in Boulder Brook basin delay the release of water to streamflow relative to Fern and Spruce Creek basins. Correlation analyses were performed to determine whether significant relations exist between component contributions to streamflow and basin physical characteristics such as slope, amount of surficial debris, and type and amount of vegetation (Table 1).

4.2. Correlation Analysis

Clow and Sueker [this issue] demonstrated that annual volume-weighted mean sodium concentrations for nine alpine/subalpine basins were positively correlated with the amount of old debris and subalpine meadow, basin characteristics that are associated with low-hydraulic-conductivity environments. Sodium was negatively correlated with steep slope, unvegetated area, and young debris, basin characteristics that are associated with the high-conductivity talus and bedrock environments. Sodium was positively correlated with silica and alkalinity, indicating a plagioclase mineral weathering control on these solutes. In lower-gradient, low-conductivity environments the residence time of water is sufficiently long for mineral weathering reactions to occur.

A similar conclusion was drawn by *Peters and Murdoch* [1985], who determined that differences in lake-water pH could be attributed to differences in the groundwater contribution to the lakes. Differences in groundwater contributions were attributed to thick till that was more extensively distributed in the neutral-lake basin than in the acidic-lake basin. In the neutral-lake basin, precipitation that percolated into the till had a residence time sufficiently long to allow the neutralization of precipitation by alkalinity-producing reactions.

In the six study basins, steeper slopes enhance, while surficial deposits impede, the direct discharge of snowmelt water to surface streams. This conclusion is supported by the significant negative correlations between seasonally averaged streamflow of the unreacted, event, and snow components contributions, as percent of total flow, and the percentage of the basin covered by old debris (Tables 1 and 5). Seasonal event contributions were positively correlated with median slope and the percent of basin with slope greater than 30° (steep slope), indicating that snowmelt water in steeper basins is routed more quickly to surface streams. Given the small data set, additional basins or additional years of data are required to test the robustness of these relations.

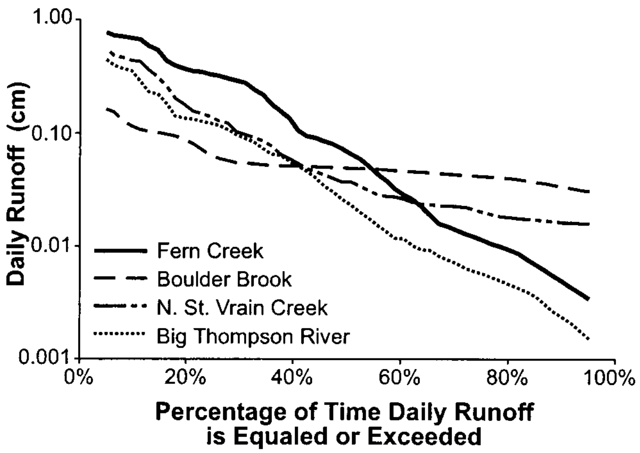

Figure 8. Flow-duration curves. Slopes of the Spruce Creek and Fall River flow-duration curves are similar to Fern Creek and Big Thompson River slopes.

Basin size had only a small effect on the response of streamflow to snowmelt and was not correlated with any of the components. Excluding Boulder Brook, 50–63% of streamflow was contributed by unreacted water on a seasonal basis; unreacted flow increased with larger basin size (Table 4). However, the increase of unreacted flow contributions with increasing basin size may be an artifact of using base flow sodium concentrations for the reacted component [*Sueker*, 1996]. In the larger basins, base flow sodium concentrations may be elevated relative to average groundwater concentrations, especially during snowmelt, causing an overestimation of the unreacted component contribution to streamflow.

Topographic and geologic characteristics were useful predictors of surface water chemistry [*Clow and Sueker*, this issue] and were correlated with component contributions to streamflow. Basins with extensive surficial debris and shallower slopes, such as Boulder Brook basin, will be the least sensitive to increases in atmospheric acid deposition. Geographic Information System map information may be useful for implementing a regional screening process to determine the sensitivity of basins to atmospheric acid deposition.

4.3. Reliability of Model Assumptions

Hydrograph separation results are affected by the assumptions made in defining components and tracers. *Rice and Horn-*

Table 5. Results of Hydrograph Separation Sensitivity Analyses for Fern Creek

	Total Runoff, cm	Snow, %	Rain, %	Subsurface, %
May	16.6	31	0	69
June	22.5	38	0	62
July	12.2	38	0	62
August	8.9	33	1	66
September	5.0	13	3	84
October	2.3	1	11	88
Total	67.5	33	1	67

berger [1998] evaluated seven pairs of commonly used tracers in a three-component hydrograph separation model for peak storm flows. Results were not always physically meaningful, suggesting that assumptions of hydrograph separation had been violated or end-member compositions had not been properly defined. As discussed in section 4.1, results of the hydrograph separation calculations in this study were physically meaningful and agreed well with proposed flow mechanisms for alpine basins. In this section, model assumptions are tested, and sensitivity analyses for component compositions are presented.

For the two-component model ((2) and (3)) the condition that tracer compositions of the two components must be distinguishable clearly is met for all basins for both the sodium and the $\delta^{18}O$ tracers (Table 2). Variations in the sodium concentrations and $\delta^{18}O$ values for the components are small compared to the variation between components. Component contributions to streamflow changed by less than $\pm 1\%$ of total streamflow when component tracer values were changed by $\pm 1\sigma$ of the measured values. The condition that only two components contribute to streamflow is met for the sodium tracer but is violated for the isotopic tracer when streamflow $\delta^{18}O$ content exceeds that of base flow in midsummer (Figure 2d).

Mast et al. [1995] found that the $\delta^{18}O$ of water collected from a snowmelt lysimeter increased from about -20 to -18.6‰ prior to the occurrence of isotopically heavier rain events. However, a constant event-water composition was determined to be reasonable, because the onset of snowmelt is not uniform over the basin because of the large elevation range [*Mast et al.*, 1995]. A sensitivity analysis using constant event-water isotopic composition was conducted to determine the effect of using different snowmelt $\delta^{18}O$ values on hydrograph separation results. Event-water contributions to streamflow decreased by up to 5% and increased by up to 8% of total streamflow for each sampling period and for the entire study period when event-water $\delta^{18}O$ changed to -20‰ and -18.6‰, respectively.

For the three-component model ((4) and (5)), components have distinct, noncollinear tracer compositions, as shown by their unique locations on the mixing diagrams, and streamflow is well defined by the mixing triangle (Figure 7). Thus the first three conditions of the three-component model are met.

Assuming a constant tracer composition equal to the mean of the base flow values for the reacted, preevent, and subsurface components introduces error into the hydrograph separation results [*Hooper and Shoemaker*, 1986; *Williams et al.*, 1993]. Base flow in Fern Creek and Boulder Brook was shown to represent average groundwater sodium concentrations. However, base flow sodium concentrations may not be a reasonable surrogate for the subsurface component at all times of the runoff season. Also, base flow is maintained by return flow from saturated subsurface reservoirs, so base flow composition may not reflect the composition of water stored in the unsaturated zone. Tremendous temporal and spatial heterogeneity exists in soil-water $\delta^{18}O$ content and sodium concentrations of samples collected from Loch Vale basin [*Arthur and Fahey*, 1993; D. W. Clow, USGS, unpublished data, 1996], and a similar heterogeneity is expected for the six study basins. Collecting representative soil-water samples for six basins would be a daunting undertaking and was beyond the scope of this project. However, in the following discussion we begin to quantify the error introduced by assuming a constant subsurface component composition.

Reacted and subsurface components are defined in this study as the average of all waters that have passed through subsurface matrices, including concentrated groundwater, soil pore water, and dilute snowmelt waters that percolate rapidly through the soils. Even though infiltrating snowmelt water may exchange sodium rapidly enough to make it indistinguishable from resident water [*Clow*, 1992], the available pool of exchange cations may decrease as snowmelt progresses, eventually decreasing the sodium concentration in the exiting subsurface water [*Campbell et al.*, 1995; *Williams et al.*, 1993]. The concentration-discharge relation of sodium observed for most basins (Figure 4) may be caused by the depletion of available exchange cations in the soil pools during snowmelt, as well as by differences in soil depth and development as a function of elevation. *Drever and Zobrist* [1992] found that concentrations of the major cations and silica in surface water decreased approximately exponentially with increasing elevation in small granitic basins in southern Switzerland. The mineral surface area exposed to weathering in the thicker soils at lower elevations was much greater than in the thin or absent soils at higher elevations, and the residence time of water in contact with weatherable minerals was greater in the thicker soils, causing the observed concentration-elevation relation.

In the study basins, melt begins at lower elevations, where soils are deeper and more developed than at higher elevations [*Clow et al.*, 1997], and soil water and groundwater may be more concentrated. As the snowmelt season progresses, the contributing area of snowmelt runoff increases, but snowmelt waters encounter thinner, less mature soils at higher elevations. Later in the snowmelt season, much of the meltwater is derived from high-elevation snowfields found in steeply sloped cirques and headwalls. Meltwaters from these areas may pass quickly through thin, poorly developed soils into surface water channels, with little opportunity to acquire solutes along the way. However, streamflow sodium concentrations increase with decreasing elevation during this time, indicating that groundwater that contains elevated sodium concentrations, with respect to stream concentrations, is discharging to the stream (Figure 5).

The isotopic compositions of subsurface waters may also change over the snowmelt and summer seasons. The mean $\delta^{18}O$ values of synoptic groundwater samples were lighter than base flow in Fern Creek and were heavier than base flow in Boulder Brook (Table 2). July synoptic groundwater $\delta^{18}O$ values were about 0.6‰ and 0.7‰ heavier in July than in August for Fern Creek and Boulder Brook, respectively, reflecting the addition of heavier summer rain. The isotopic composition of stream water synoptic samples collected from Fern Creek basin in August was, on average, about 1.3‰ heavier than the composition of samples collected in July. Lower-elevation samples were heavier than higher-elevation samples, indicating contributions of heavier water from lower in the basin (Figure 5). Eventually, the isotopic composition of water in subsurface matrices may stabilize or begin to decrease as snowstorms in late summer and early fall contribute lighter water to the basin.

Three-component hydrograph separations were performed for Fern Creek to evaluate the effects of variable isotopic and chemical compositions of subsurface waters. The variation in tracer values (Figure 9) was developed to reflect changes in basin-wide average subsurface water sodium concentrations and $\delta^{18}O$ values that may occur [*Clow and Drever*, 1996; *Sueker*, 1996]. Fern Creek was chosen for this analysis because of the known hysteresis in sodium concentrations and because syn-

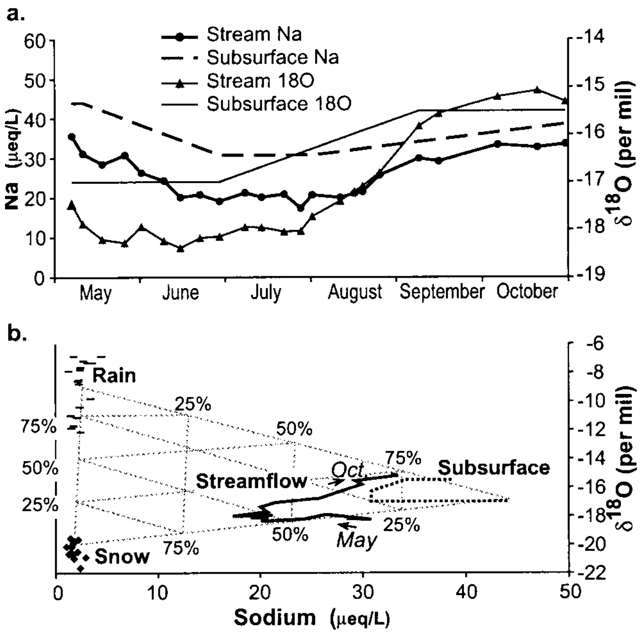

Figure 9. Fern Creek sensitivity analysis with varying subsurface component sodium concentrations and $\delta^{18}O$ values: (a) model inputs and (b) mixing diagram.

optic data were available. Synoptic data were also available for Boulder Brook, but there was no hysteresis in sodium concentrations, and streamflow sodium and $\delta^{18}O$ values were tightly grouped around base flow values at all times of the melt period (Figure 7).

Estimated subsurface contributions increased, and contributions from rain and snow decreased for all months when variable subsurface tracer values were used for Fern Creek (Table 6 and Figure 9). Overall seasonal contributions to total streamflow changed from 47% to 33% for snowmelt, from 5% to 1% for rain, and from 54% to 67% for subsurface water. These results agree reasonably well with *Williams et al*. [1993], who performed sensitivity analyses of hydrograph separation calculations for streamflow in a small alpine basin. They determined that subsurface contributions to streamflow during snowmelt changed from ~41% to ~62% of total flow when the subsurface component tracer value was changed from a constant value based on base flow silica concentration to a piecewise linear value based on soil-water silica concentrations.

Given the hysteresis in chemical concentrations and elevational variations in soil depth and development, using variable subsurface component tracer concentrations is more reasonable than using constant tracer values. Determining how to vary the component tracer values without direct measurements is problematic. *Rice and Hornberger* [1998] demonstrate that flow components cannot be unambiguously identified using chemical and (or) isotopic measurements alone and discuss the importance of combining hydrometric and hydrochemical measurements to perform meaningful hydrograph separations. However, collecting representative subsurface samples across hundreds of square kilometers of rugged alpine terrain is impractical. As a first step in comparing the hydrologic response to snowmelt for a number of collocated alpine/subalpine basins, using constant subsurface component tracer values in hydrograph separation models is a reasonable approach.

5. Conclusions

Alpine/subalpine basins are sensitive environments that should be protected from acidic atmospheric deposition to maintain good water quality and healthy ecosystems. Of the six basins described in this study, Boulder Brook is the least sensitive to increased acidic deposition, because large quantities of unconsolidated surficial material are available to neutralize acidic deposition. The remaining basins are more sensitive to increases in acidic deposition, especially in the higher-elevation areas where soils are typically thinnest and least developed and during the summer when subsurface reservoirs of base cations are most depleted.

Basin size had little or no effect on the routing of precipitation water through the basins. Old debris was correlated with contributions from preevent, reacted, and subsurface components, indicating that the debris provides storage capacity that

Table 6. Spearman Correlation Coefficients for Relations Between Basin Physical Characteristics and Monthly and Seasonal Component Contributions to Streamflow

Month	Component	Old Debris	Average Elevation	Median Slope	Steep Slope	Area	Unvegetated	Subalpine Meadow	Young Debris
May	event	−0.94							
	snow	−0.77							
June	event	−0.97	−0.62	0.64	0.51				
	snow	−0.70							
July	unreacted	−0.46							
	event	−0.49	−0.83	0.82	0.93				
	snow	−0.71							
	rain					0.87			
August	unreacted	−0.60	−0.77						
	rain					0.93			
September	unreacted	−0.60	−0.77						
	rain	−0.50							
October	unreacted	−0.61	−0.93		0.60				
	rain				0.81		0.81	−0.88	0.85
Season	unreacted	−0.55							
	event	−0.93		0.63	0.50				
	snow	−0.70							

Relations between event and preevent and unreacted and reacted are equal but opposite in sign. Relations between snow and subsurface are similar but opposite in sign. Numbers are r values; only significant relations ($p < 0.05$) are shown.

delays flow, which increases residence times and sodium concentrations. Event water was correlated with steep slope, indicating that snowmelt is delivered rapidly to surface flow in high-gradient basins.

Hydrograph separation results provided insight into the generation of streamflow in the six alpine/subalpine basins during snowmelt and provided a means to compare the responses of these different basins. During early snowmelt, water that was resident in subsurface matrices prior to snowmelt was flushed into the surface water system. For most basins this resident water was rapidly replaced by snowmelt, and surface flow of melting snow became increasingly important. From May through August, 42–57% of total streamflow was provided from water with a composition of snow, and 37–54% was provided by water with the composition of subsurface water. With the exception of North St. Vrain Creek, rain did not contribute substantially to streamflow until late in the melt season. However, rain contributions in all basins were small, 4–13% of total streamflow during the study period, compared to overall snowmelt and subsurface water contributions. Streamflow in Boulder Brook was dominated by contributions from subsurface waters during the entire study period. The use of constant base flow tracer values for the subsurface component underestimates contributions from subsurface sources but is sufficient for comparing component contributions to streamflow for multiple collocated basins.

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References

Arthur, M. A., and T. J. Fahey, Controls on soil solution chemistry in a subalpine forest in north central Colorado, *Soil Sci. Soc. Am. J.*, *57*, 1122–1130, 1993.

Baron, J. (Ed.), *Biogeochemistry of a Subalpine Ecosystem*, Springer-Verlag, New York, 1992.

Baron, J., and D. H. Campbell, Nitrogen fluxes in a high-elevation Colorado Rocky Mountain basin, *Hydrol. Processes*, *11*, 783–799, 1997.

Baron, J. S., D. S. Ojima, E. A. Holland, and W. J. Parton, Analysis of nitrogen saturation potential in Rocky Mountain tundra and forest: Implications for aquatic systems, *Biogeochemistry*, *27*, 61–82, 1994.

Barry, P. J., and A. G. Price, Short-term changes in the fluxes of water and of dissolved solutes during snow-melt, in *Seasonal Snowcovers: Physics, Chemistry, Hydrology*, edited by H. G. Jones and W. J. Orville-Thomas, pp. 501–530, D. Reidel, Norwell, Mass., 1987.

Bottomley, D. J., D. Craig, and L. M. Johnston, Oxygen-18 studies of snowmelt runoff in a small Precambrian shield watershed: Implications for streamwater acidification in acid-sensitive terrain, *J. Hydrol.*, *88*, 213–234, 1986.

Braddock, W. A., and J. C. Cole, Geologic map of Rocky Mountain National Park and vicinity, Colorado, *U.S. Geol. Surv*. Map, *I-1973*, 1990.

Caine, N., Diurnal variations in the inorganic solute content of water draining from an alpine snowpatch, *Catena*, *16*, 153–162, 1989a.

Caine, N., Hydrograph separation in a small alpine basin based on inorganic solute concentrations, *J. Hydrol.*, *112*, 89–101, 1989b.

Campbell, D. H., D. W. Clow, G. P. Ingersoll, M. A. Mast, N. E. Spahr, and J. T. Turk, Processes controlling the chemistry of two snowmelt-dominated streams in the Rocky Mountains, *Water Resour. Res.*, *31*(11), 2811–2821, 1995.

Campbell, D. H., J. S. Baron, K. A. Tonnessen, P. D. Brooks, and P. F. Schuster, Controls on nitrogen flux in alpine/subalpine watersheds of Colorado, *Water Resour. Res.*, this issue.

Clow, D. W., Weathering rates from field and laboratory experiments on naturally weathered soils, Ph.D. thesis, Univ. of Wyom., Laramie, 1992.

Clow, D. W., and J. I. Drever, Weathering rates as a function of flow through an alpine soil, *Chem. Geol.*, *132*, 131–141, 1996.

Clow, D. W., and J. K. Sueker, Relations between basin characteristics and stream water chemistry in alpine/subalpine basins in Rocky Mountain National Park, Colorado, *Water Resour. Res.*, this issue.

Clow, D. W., M. A. Mast, T. D. Bullen, and J. T. Turk, Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an alpine/subalpine watershed, Loch Vale, Colorado, *Water Resour. Res.*, *33*(6), 1335–1351, 1997.

Dincer, T., B. R. Payne, T. Florkowski, J. Martinec, and E. Tongiorgi, Snowmelt runoff from measurements of tritium and oxygen 18, *Water Resour. Res.*, *6*(1), 110–124, 1970.

Drever, J. I., and J. Zobrist, Chemical weathering of silicate rocks as a function of elevation in the southern Swiss Alps, *Geochim. Cosmochim. Acta*, *56*, 3209–3216, 1992.

Durka, W., E. D. Schule, G. Gebauer, and S. Voerkelius, Effects of forest decline on uptake and leaching of deposited nitrate determined from N-15 and O-18 measurements, *Nature*, *372*, 765–767, 1994.

Eilers, J. M., et al., Data compendium for selected physical and chemical variables, in *Western Lake Survey*, *Phase I*: *Characteristics of Lakes in the Western United States*, vol. 2, *Rep. EPA-600/3-86/054a*, U.S. Environ. Prot. Agency, Washington, D. C., 1987.

Eshleman, K. N., J. S. Pollard, and A. Kuebler O'Brien, Determination of contributing areas for saturation overland flow from chemical hydrograph separations, *Water Resour. Res.*, *29*(10), 3577–3587, 1993.

Eshleman, K. N., T. D. Davies, M. Tranter, and P. J. Wigington, A two-component mixing model for predicting regional episodic acidification of surface waters during spring snowmelt periods, *Water Resour. Res.*, *31*(4), 1011–1021, 1995.

Finley, J. B., and J. I. Drever, Chemical hydrograph separation using field and experimental data with implications for solute cycling in an alpine catchment, in *Water-Rock Interaction*, edited by Y. K. Kharaka and A. S. Maest, pp. 553–556, A. A. Balkema, Brookfield, Vt., 1992.

Fritz, P., J. A. Cherry, K. U. Weyer, and M. Sklash, Storm runoff analyses using environmental isotopes and major ions, in *Interpretation of Environmental Isotopes and Hydrochemical Data in Underground Hydrology*, pp. 111–130, Int. At. Energy Agency, Vienna, 1976.

Hinton, M. J., S. L. Schiff, and M. C. English, Examining the contributions of glacial till water to storm runoff using two- and three-component hydrograph separations, *Water Resour. Res.*, *30*(4), 983–993, 1994.

Hooper, R. P., and C. A. Shoemaker, A comparison of chemical and isotopic hydrograph separation, *Water Resour. Res.*, *22*(10), 1444–1454, 1986.

Landers, D. H., et al., Population descriptions and physico-chemical relationships, in *Western Lake Survey*, *Phase I*: *Characteristics of Lakes in the Western United States*, vol. 1, *Rep. EPA-600/3-86/054a*, U.S. Environ. Prot. Agency, Washington, D. C., 1987.

Lynch, J. A., J. W. Grimm, and V. C. Bowersox, Trends in precipitation chemistry in the United States: A national perspective, 1980–1992, *Atmos. Environ.*, *29*(11), 1231–1246, 1995.

Mast, M. A., C. Kendall, D. H. Campbell, D. W. Clow, and J. Back, Determination of hydrologic pathways in an alpine-subalpine basin using isotopic and chemical tracers, Loch Vale watershed, Colorado, USA, in *Biogeochemistry of Seasonally Snow-Covered Catchments*, edited by K. A. Tonnessen, M. W. Williams, and M. Tranter, *IAHS Publ.*, *228*, 263–270, 1995.

McDonnell, J. J., M. K. Stewart, and I. F. Owens, Effect of catchment-scale subsurface mixing on stream isotopic response, *Water Resour. Res.*, *27*(12), 3065–3073, 1991.

McNamara, J. P., D. L. Kane, and L. D. Hinzman, An analysis of streamflow hydrology in the Kuparuk River Basin, Arctic Alaska: A nested watershed approach, *J. Hydrol.*, *206*, 39–57, 1998.

Michel, R. L., and J. T. Turk, Use of sulphur-35 to study rates of sulphur migration in the Flat Tops Wilderness Area, Colorado, in *Isotopes in Water Resources Management*, pp. 293–301, Int. At. Energy Agency, Vienna, 1995.

Moore, R. D., Tracing runoff sources with deuterium and oxygen-18 during spring melt in a headwater catchment, southern Laurentians, Quebec, *J. Hydrol.*, *112*, 135–148, 1989.

Peters, N. E., and P. S. Murdoch, 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, 1985.

Rice, K. C., and G. M. Hornberger, Comparison of hydrochemical tracers to estimate source contributions to peak flow in a small, forested, headwater catchment, *Water Resour. Res*., *34*(7), 1755–1766, 1998.

Rodhe, A., Spring flood meltwater or groundwater?, *Nord. Hydrol*., *12*, 21–30, 1981.

Rodhe, A., Snowmelt-dominated systems, in *Isotope Tracers in Catchment Hydrology*, edited by C. Kendall and J. J. McDonnell, chap. 12, pp. 391–434, Elsevier, New York, 1998.

Shanley, J. B., and N. E. Peters, Preliminary observations of streamflow generation during storms in a forested Piedmont watershed using temperature as a tracer, *J. Contam. Hydrol*., *3*, 349–365, 1988.

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

Soil Conservation Service, Colorado Annual data summary of federal-state-private cooperative snow surveys, report, U.S. Dep. of Agric., Lakewood, Colo., 1994.

Sueker, J. K., Chemical hydrograph separation during snowmelt for three headwater basins in Rocky Mountain National Park, Colorado, in *Biogeochemistry of Seasonally Snow-Covered Catchments*, edited by K. A. Tonnessen, M. W. Williams and M. Tranter, *IAHS Publ*., *228*, 271–281, 1995.

Sueker, J. K., Isotopic and chemical flowpath separation of streamflow during snowmelt and hydrogeologic controls of surface-water chemistry in six alpine-subalpine basins, Rocky Mountain National Park, Colorado, Ph.D. thesis, Univ. of Colo., Boulder, 1996.

Sueker, J. K., R. L. Michel, and J. T. Turk, Use of cosmogenic sulfur-35 for comparing ages of water from three alpine-subalpine basins in the Colorado Front Range, *Geormorphology*, *27*(1–2), 61–74, 1999.

Tranter, M., P. W. Abrahams, I. Blackwood, T. D. Davies, P. Brimblecombe, I. P. Thompson, and C. E. Vincent, Changes in streamwater chemistry during snowmelt, in *Seasonal Snowcover: Physics, Chemistry, Hydrology*, edited by H. G. Jones and W. J. Orville-Thomas, pp. 575–597, D. Reidel, Norwell, Mass., 1987.

Turk, J. T., and N. E. Spahr, Rocky Mountains, in *Acidic Deposition and Aquatic Ecosystems*, edited by D. F. Charles, pp. 471–501, Springer-Verlag, New York, 1991.

Ugland, R. C., W. S. Maura, R. D. Steger, and G. B. O'Neill, Water resources data, Colorado, Water Year 1994, Volume 1, Missouri River Basin, Arkansas River Basin and Rio Grande Basin, *Rep. CO-94-1*, U.S. Geol. Surv., Denver, Colo., 1994.

Wels, C., R. J. Cornett, and B. D. LaZerte, Groundwater and wetland contributions to stream acidification: An isotopic analysis, *Water Resour. Res*., *26*(12), 2993–3003, 1990.

Williams, M. W., and J. M. Melack, Solute chemistry of snowmelt and runoff in an alpine basin, Sierra Nevada, *Water Resour. Res*., *27*(7), 1575–1588, 1991.

Williams, M. W., A. D. Brown, and J. M. Melack, Geochemical and hydrologic controls on the composition of surface water in a high-elevation basin, Sierra Nevada, California, *Limnol. Oceanogr*., *38*(4), 775–797, 1993.

Zeman, L. J., and H. O. Slaymaker, Hydrochemical analysis to discriminate variable runoff source areas in an alpine basin, *Arct. Alp. Res*., *7*(4), 341–351, 1975.

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