CHEMICAL HYDROGRAPH SEPARATION USING FIELD AND EXPERIMENTAL DATA WITH IMPLICATIONS FOR SOLUTE CYCLING IN AN ALPINE CATCHMENT

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Chemical hydrograph separation using field and experimental data with implications for solute cycling in an alpine catchment

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ABSTRACT: Geochemical reactions during bedrock fracture flow and in the soil column alter input solute concentrations in the West Glacier Lake catchment. Chemical hydrograph separation provides information regarding the relative importance of geochemical processes. Soil column reactions include cation exchange, anion retention, biotic uptake/release, and mineral weathering. Solute concentrations in precipitation are relatively constant; thus, seasonal concentrations in soil solutions are controlled by cation exchange and anion retention while net flux of cations from the catchment is the result of mineral weathering.

1 INTRODUCTION

Concentrations of solutes discharged from the West Glacier Lake (WGL) catchment in the Snowy Range, southeastern Wyoming represent a delicate balance between geochemical processes and input chemistry. Solute fluxes from the alpine WGL basin are very sensitive to changes in precipitation chemistry mostly as a result of thin, immature soils that are sparsely distributed over the catchment. In catchments where the chemistry of precipitation is, and has been, fairly constant, the flux of cations on an annual basis stems from mineral weathering rather than supply from cation exchange (Mast et al., 1990). Conversely, seasonal patterns of solute concentrations in surface waters within the WGL catchment are governed by (1) exchange reactions in the soil, (2) dilution during snowmelt, and (3) bedrock discharge.

Chemical hydrograph separation has long been employed to trace the relative contribution of discharge sources in catchments (Pinder and Jones, 1969; Robson and Neal, 1990). In this study, the technique is applied to investigate the seasonal variation in solute concentrations in the Meadow Creek tributary of West Glacier Lake (Fig. 1).

2 SITE DESCRIPTION

The West Glacier Lake catchment is an alpine basin (91 ha) with elevation ranging from 3276 m to 3500 m. Bedrock geology consists of Precambrian quartzite cross-cut by amphibolite dikes. Glacial and periglacial action formed the present basin morphology, with talus slopes and rock outcrops dominating the terrain. Soils are thin and immature occupying localized topographic depressions. Vegetation ranges from subalpine fir (Abies lasiocarpa), at low elevation, to a willow-krummholz assemblage at higher elevation. Grassy meadows occupy narrow zones adjacent to the creek. Snowfall supplies 80-90% of the annual precipitation input (in water equivalence) with spring snowmelt beginning in late March and lasting until late June. Four tributaries drain into WGL (Fig. 1). Meadow Creek discharge consists of melt-water early in the year, spring discharge during late summer, then no flow as the bedrock aquifer system drains below the elevation of the spring.

3 METHODS

Precipitation volume and chemistry are measured at a National Acid Deposition

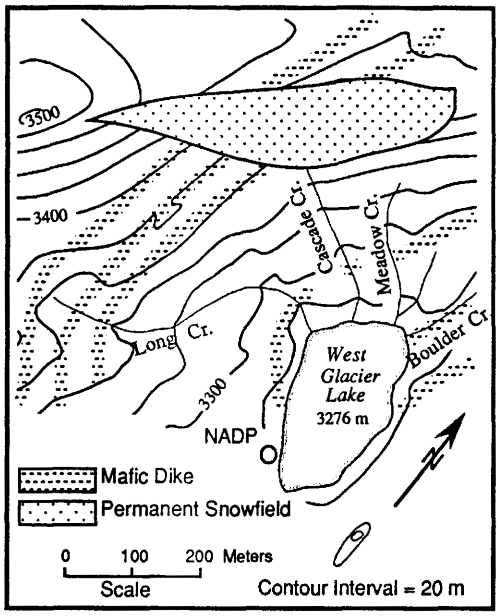

Fig. 1 Location map for West Glacier Lake and surrounding environs.

Program station on the southwest side of WGL. Discharge is measured in Meadow Creek by a Parshall flume and water-level recorder. Five tension lysimeter nests (3-6/site) were installed in the soil of the Meadow Creek catchment, and fitted with extension tubes to allow sampling through the snowpack. Snow lysimeters consisted of large plastic sheets (2 x 2) placed on the ground to intercept snowmelt prior to contacting the soil. Once snowmelt began, pits were dug to access the snow lysimeter outlet. Samples were collected twice weekly from the lysimeters and creek throughout the snowmelt season (March-June). Major cations were measured in filtered, acidified samples by flame AA, and major anions were measured in filtered samples by ion chromotography. Alkalinity was determined by Gran titration to pH 3.5.

Chemical hydrograph separation for a two component system relies on mass conservation leading to:

$$Q_S = Q\frac{(C - C_g)}{(C_S - C_g)} \qquad (1)$$

where C_S, C_g are solute concentrations in surface and soil pore-water, respectively; C is the concentration measured in the creek; and Q_S, Q_g, Q are volumes discharged as surface, soil pore-water, and total, respectively. Since Eq (1) is written assuming mixing within a fixed volume, an alternative equation can be used when discharge is not available (common during early snowmelt):

$$C = xC_S + (1-x)C_g \qquad (2)$$

where C, C_S, and C_g are as defined in Eq (1), and x is the mass fraction of solute from snowmelt contributing directly to the creek without interaction with the soil or bedrock.

4 WATER CHEMISTRY

Solute concentrations in the snow, soil pore-water, and creek are plotted as time series in Figure 2. The concentration of Ca in the snow begins quite high then drops rapidly, ultimately crossing the curve for the creek. Cross-over of concentration is indicative of the way in which the snowpack melts; the process probably involves differential maturation of the snowpack as a function of elevation, aspect, and slope (Dozier et al., 1987). An elevation gradient in snowpack melting is consistent with the placement of our snow lysimeters, which were located at a low elevation in the catchment.

A similar pattern is shown for SO_4. The main difference is that the soil pore-water concentration of SO_4 is less than Ca by a factor of 4, and remains nearly constant at ~10 µeq/l. Although interpolation of snowmelt data early in the season introduces uncertainty in the exact pattern, the linear segment is a reasonable first approximation. The cross-over for Ca and SO_4, between snowmelt and the creek, occurs on the same date, which is consistent with the abundance of each in the snowpack.

Silica concentrations in snowmelt, soil pore-water, and creek remain separate because there is no labile source of SiO_2 in the snowpack. Stream concentrations follow closely the pattern of soil pore-water.

Laboratory determinations of exchangeable Ca and inorganic SO_4, along with estimates of the total mass of soil in the Meadow Creek tributary, indicate that the exchange pools in the soil are much greater than the average

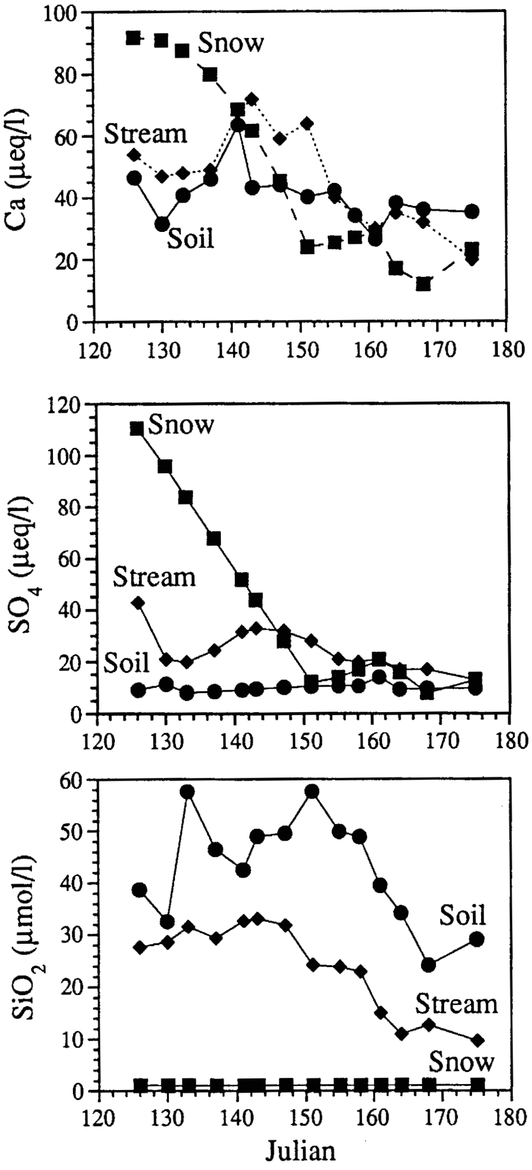

Fig. 2 Time series for Ca, SO4, and SiO_2 concentrations in snowmelt, soil pore-water, and stream.

annual flux of solutes from the soil. The difference is a factor of 30 for Ca, and a factor of 5 for SO4. In soil pore-water solutions, Ca is affected by cation exchange reactions under the dilute conditions of WGL, while SO4 is subject to anion retention in the soil. Once generated in the soil, SiO_2 should behave the most conservatively.

5 HYDROGRAPH SEPARATION

Chemical hydrograph separations were calculated using Ca, SO4, and SiO_2 as a measure of the relative mass contribution from snowmelt and soil pore-water (Fig. 3). There are no discharge data prior to Julian day 152, thus Eq (2) is the most appropriate model. The calculation provides instantaneous estimates of the mass fraction (x) using the solute concentrations in snowmelt, soil pore-water, and creek. The apparent fraction of soil pore-water ranges from 60-90% at the beginning of snowmelt; an unexpected result since initial snowmelt contains high concentrations of solutes from preferential elution of the snowpack (Bales, et al., 1990). Percent soil water calculated from Ca and SO4 decreases rapidly because solute concentrations in snowmelt and soil pore-water converge, and the hydrograph separation becomes poorly defined. Silica, however, indicates a more sustained influence from soil pore-water than either Ca or SO4 because the snowpack contains no SiO_2.

The results obtained from the chemical hydrograph separation offer additional information with which to interpret the time series shown in Figure 2. Beyond the first cross-over point for Ca, Eq (2) no longer applies since the creek is, by definition, intermediate in concentration between the snow and soil pore-water. Assuming the solutes in snowpack are distributed homogeneously, a similar chemical hydrograph for Ca and SO4 should develop, shifted in time as snowpack at higher elevations begins melting. The concentration of Ca and SO4 in the creek remains closer to soil pore-water concentrations, an indication of the strong influence soil pore-water, and soil processes, has on stream chemistry.

Later in the season, another cross-over point occurs for the Ca and SO4 hydrographs where soil pore-water concentrations exceed that of the creek. At this time, creek chemistry is controlled by dilution from the large volume of water supplied when the entire snowpack is melting.

6 CONCLUSIONS

Chemical hydrograph separation provides a

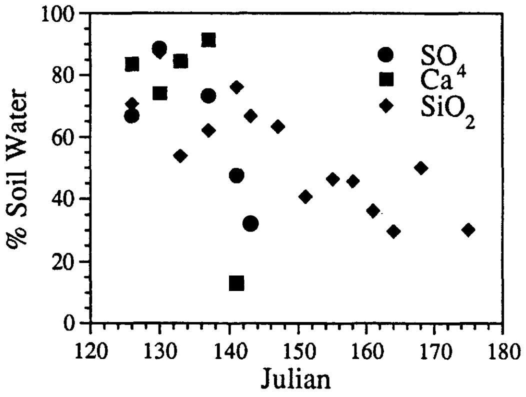

Fig. 3 Result of chemical hydrograph separation shown as percent soil pore-water.

method to investigate the relative importance of geochemical processes during snowmelt in the WGL catchment. Soil processes of cation exchange and anion retention control the chemistry of stream water even with preferential elution of solutes from the snowpack. Although concentrations of Ca and SO4 in the soil are controlled by cation exchange and anion retention on a seasonal basis, the annual flux of solutes from the catchment is due to mineral weathering.

7 ACKNOWLEDGEMENT

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