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Chemical mixing model of streamflow generation at La Selva Biological Station, Costa Rica

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Abstract

La Selva Biological Station occupies an area of lowland tropical rainforest in central Costa Rica. Sodium and chloride data were used to quantify the mixing proportions of local runoff and geothermal groundwater at several sites throughout the stream channel system in late April, at the end of the dry season. The fraction of streamflow accounted for by geothermal groundwater varied spatially between 0 and 0.85, indicating a significant contribution to streamflow and to stream solute loads from geothermal groundwater at some sites. In general, higher inputs of geothermal groundwater were found at lower elevations. Over half the flow from one basin (the Salto) was due to geothermal groundwater, suggesting a minimum annual runoff of about 0.7 m of geothermal groundwater from this basin. A plot of Na/Cl vs. fraction of geothermal groundwater revealed watershed-scale chemical differences between the two major drainage systems (the Sura and the Salto), differences that were not apparent from a traditional two-solute plot of Cl vs. Na concentration. A small (21 mm) storm produced relatively little change in mixing proportions, as most throughfall was apparently retained in the relatively dry soils. © 1997 Elsevier Science B.V.

Keywords: Geochemistry; Geothermal systems; Groundwater; Rivers and streams; Runoff; Streamflow

1. Introduction

La Selva Biological Station occupies an area of lowland tropical rainforest in central Costa Rica. Previous research focusing on in-stream ecological processes at La Selva led to the discovery of high concentrations (up to 300 ppb) of soluble reactive phosphorous

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(SRP) in streamwater (Pringle et al., 1990; Pringle, 1991). High SRP concentrations were correlated with high concentrations of major ions (Pringle et al., 1990). The most likely source of these high solute concentrations is the discharge of geothermal groundwater to streams. In this paper we present new chemical analyses in the context of a chemical mixing model which shows the proportions of streamflow generated by local runoff (drainage of hillslopes at La Selva) and by discharge of geothermal groundwater. The large difference in solute concentrations between the two hydrologically-distinct water sources provides an ideal situation for the application of a chemical mixing model. The main points of this paper are the large magnitude of the geothermal groundwater discharge and its variability in space, the implications for water and solute budgets on this tropical volcanic landscape, and the documentation of significant interbasin differences in the behaviour of "conservative" solutes often used in hydrochemical mixing models (including application of a mixing diagram that appears to be more sensitive than a traditional two-solute diagram to non-conservative behavior).

2. Study site

2.1. General features

La Selva Biological Station (Fig. 1), owned and operated by the Organization for Tropical Studies, is located near the base of Costa Rica's Cordillera Central, in the transitional zone between the Caribbean coastal plain and the steep foothills. The 3300 ha preserve forms the downslope end of a tract of primary rain forest that extends over 30 km to the south, through Braulio Carrillo National Park and up the north slope of Volcan Barva (Pringle, 1988). From 1963 to 1991 La Selva received an average of 3,962 mm of precipitation per year (Sanford et al., 1994). February, March, and April are the dryest months of the year, averaging about 170 mm of precipitation per month. Annually, evapotranspiration accounts for about 47% of precipitation at La Selva (Luvall, 1984). The Sura and Salto are the major streams draining La Selva. At present streamflow is not continuously recorded and there are no permanent flow measurement structures (weirs or flumes) on any of the streams at La Selva.

Pleistocene lava flows form the bedrock at La Selva (Alvarado, 1985). The Salto basaltic andesite is the older of the two main flows at La Selva; the younger andesitic Esquina flow overlies the Salto in two large areas, in the center (between the Salto and Sura streams) and along the eastern margin (east of the Pantano stream) of La Selva. One or both of these flows may be present beneath the younger alluvium which occupies the northern side of the preserve, adjacent to the Rio Puerto Viejo and Rio Sarapiqui. The two major soil orders at La Selva are Ultisols (45% of land area; mainly Typic Tropohumults) and Inceptisols (55% of land area; various suborders) (Sollins et al., 1994). There are small areas of Entisols (less than 0.5% of land area) near the Rio Sarapiqui. Ultisols cover most of the area over the Salto and Esquina lava flows, with the exception of valley bottoms. Inceptisols are found in the valley bottoms and on the alluvium occupying the northern portion of the preserve.

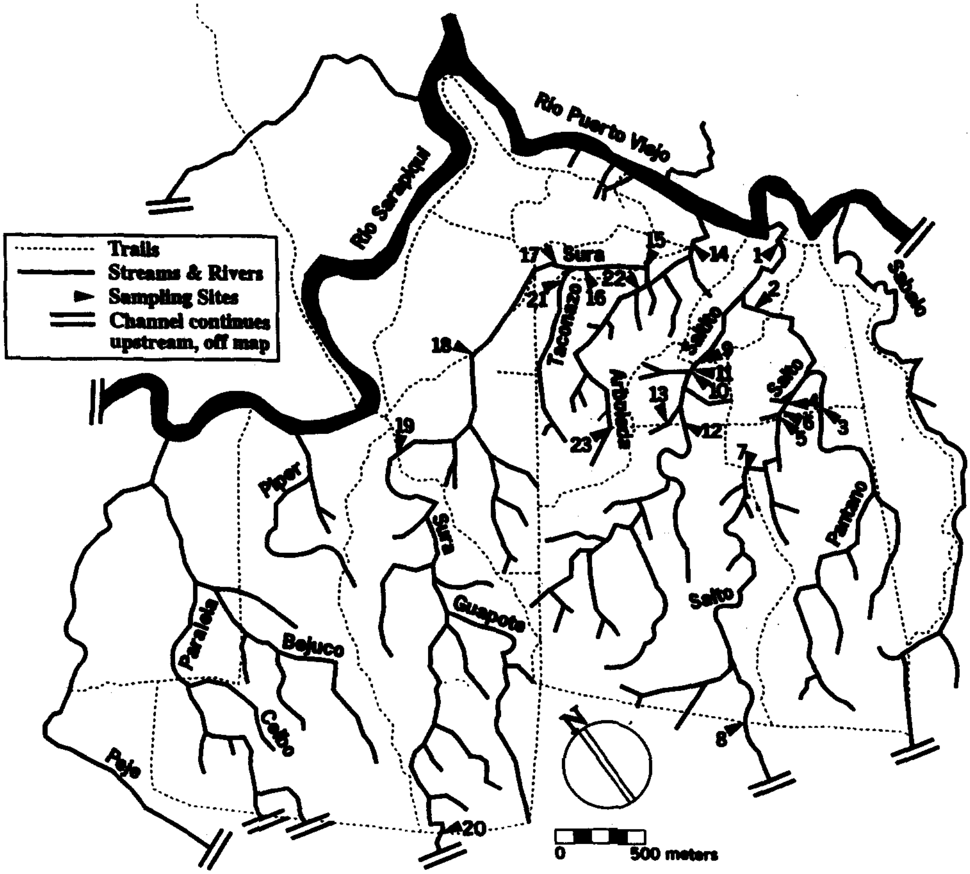

Fig. 1. Map of La Selva Biological Station, with numbered stream sampling sites (numbers correspond to those in first column of Table 1). The large spring representing geothermal groundwater is just off the map to the southeast.

2.2. *Stream chemistry*

Previous work at La Selva has documented extreme differences in the chemical composition of surface water over relatively short distances (Pringle et al., 1990, 1993; Genereux and Pringle, 1994). Seepage points a few hundred meters apart on the banks of the Salto had SRP (soluble reactive phosphorus) contents of 14 ppb and 236 ppb when sampled in 1988 (Pringle et al., 1990). When sampled in April 1994, the Cl content of streamwater in the Salto varied (spatially) from about 0.05 to over 0.5 mM (see Table 1 and discussion below). High concentrations of other ions (Na, Ca, Mg, SO_4) are correlated with high concentrations of Cl and SRP (Pringle et al., 1990). Most likely these high-solute waters originate from the interaction of groundwater with volcanic rocks and fluids at elevated temperatures, upslope and to the south in the vicinity of Volcan Barva. The resultant solute-rich groundwater (referred to here as "geothermal groundwater") then

Table 1
Chemical data for samples collected at La Selva Biological Station, 27–29 April 1994

Sample	Cl (mM)	Na (mM)	f_{gt} (based on Cl)	f_{gt} (based on Na)	Na/Cl (molar)
23	0.058	0.077	0.006	0.004	1.332
13	0.063	0.070	0.013	0	1.116
21a	0.059	0.080	0.008	0.006	1.349
21b	0.086	0.091	0.043	0.012	1.059
19a	0.053	0.077	0	0.004	1.451
19b	0.064	0.080	0.014	0.006	1.245
20	0.069	0.095	0.021	0.014	1.370
2L	0.498	1.049	0.578	0.560	2.106
2R	0.507	1.056	0.590	0.564	2.082
9L	0.311	0.637	0.335	0.324	2.047
9R	0.316	0.634	0.341	0.323	2.009
10	0.310	0.633	0.334	0.322	2.043
11	0.428	0.899	0.487	0.474	2.099
1L	0.495	1.015	0.574	0.541	2.051
1R	0.489	1.012	0.566	0.539	2.068
12	0.314	0.630	0.339	0.321	2.008
5L	0.484	0.995	0.559	0.529	2.057
5R	0.486	1.001	0.562	0.532	2.060
6	0.704	1.458	0.845	0.794	2.071
4	0.519	1.062	0.605	0.567	2.045
3	0.272	0.531	0.284	0.264	1.953
8	0.054	0.103	0.002	0.019	1.892
15a	0.239	0.594	0.242	0.300	2.485
7	0.461	0.960	0.530	0.509	2.082
14a	0.308	0.701	0.331	0.361	2.277
15b	0.241	0.580	0.245	0.292	2.403
16a	0.237	0.571	0.239	0.287	2.412
17a	0.243	0.578	0.246	0.291	2.383
18a	0.247	0.591	0.252	0.298	2.393
22a	0.437	0.936	0.499	0.496	2.141
14b	0.291	0.636	0.310	0.324	2.183
15c	0.236	0.561	0.237	0.281	2.381
16b	0.227	0.518	0.226	0.256	2.282
17b	0.248	0.559	0.253	0.280	2.255
18b	0.219	0.488	0.216	0.239	2.228
22b	0.402	0.811	0.453	0.424	2.018
24	0.820	1.808	0.996	0.994	2.205
24	0.826	1.828	1.004	1.006	2.212

f_{gt}, the fraction of geothermal groundwater, is discussed in the text.
Sample numbers refer to the numbered sites on Fig. 1. Sample numbers followed by "a", "b", or "c" indicate multiple samples collected at a single site in the Sura basin, with "a" samples being pre-storm and "b" post-storm, except for site 15 where both "a" and "b" were pre-storm and "c" was post-storm (for the 29 April 1994 storm; see abstract). Sample numbers followed by "L" and "R" indicate samples collected near the left and right banks, respectively, of the stream. Close agreement between "L" and "R" samples indicates that a one-dimensional view of stream chemistry (with concentration varying only longitudinally, along channels) is appropriate.

The two samples labeled 24 were taken at the same time and place (the large spring just off Fig. 1 to the south), and represent geothermal groundwater (see text).

flows downslope and discharges at streams within La Selva (Pringle et al., 1990, 1993). Published evidence in favor of this interpretation includes the following.

1. High SRP concentrations are associated with high concentrations of Si and base cations (Na, Ca, Mg, Mn, Sr), indicating that the phosphorus is most likely derived from rock weathering rather than mineralization of organic matter in or near the streams (Pringle et al., 1990).
2. High-solute stream waters at La Selva, classified as dilute Na–Cl–HCO_3 waters in the classification of geothermal waters proposed by White (1957), are found in many areas of geothermal activity in Costa Rica (Paniagua and VanderBilt, 1979; Bigot and Barquero, 1986) and elsewhere (Pringle, 1991). For example, rivers and lakes with elevated phosphorus content are found in volcanic terrains in Africa (Talling and Talling, 1965; Golterman, 1973; Lesack et al., 1984). As noted by Pringle et al. (1993) (p. 767) "It is common for Na–Cl waters [similar to those at La Selva but lower in bicarbonate] to be discharged at the base of a volcano at great distances from upflow areas where acid–SO_4 waters may occur (Henley, 1985), particularly in regions of local high relief and lower permanent water tables typical in tropical areas (Henley and Ellis, 1983). This discharge explains the relatively localized occurrence of dilute Na–Cl–HCO_3 waters at [La Selva, near] the base of Barva...", about 30 km downslope from a high-elevation (2000 m) acid–SO_4 spring on Barva volcano.
3. Streams draining the moderately active Poas volcano in Costa Rica showed elevated Si concentrations (47 ppm) similar to Si concentrations at seepage points along the Salto River at La Selva (50–54 ppm) (Brantley et al., 1987; Pringle et al., 1990), demonstrating the relationship between elevated Si and geothermal activity in the area. However, Cl was significantly higher at Poas than at La Selva (18.9 mM vs., at most, 0.8 mM).

2.3. *Chemical mixing model*

Chemical mixing models have become common tools in the analysis of runoff (for example, Pinder and Jones, 1969; Hooper et al., 1990; Genereux and Hemond, 1990; Kleissen et al., 1990; Robson and Neal, 1990; Neal et al., 1990; Wels et al., 1991; Genereux et al., 1993; Mulholland, 1993). These models use naturally-occurring differences in chemical concentrations (for at least one solute) to quantitatively determine the proportions in which different waters contribute to streamflow. They are "mixing" models in the sense that streamflow is viewed as mixture of two or more waters (called components or end-members) which can be distinguished chemically (and, hopefully, hydrologically). Thus, in a two component mixing model the solute tracer content of the components is related to that of streamwater by:

$$f_1 = \frac{(C_s - C_2)}{(C_1 - C_2)} \quad (1)$$

where f_1 is the fraction of streamflow accounted for by water from component 1, C_x is the tracer concentration in water x, and the subscripts 1, 2, and s designate components 1 and 2, and streamwater, respectively. The very large spatial variability in solute concentrations at La Selva makes it an ideal site for investigation of streamflow generation using a chemical mixing model. It appears that there are significant contributions to streamflow from two hydrologically and chemically distinct waters: high-solute geothermal groundwater (originating, as noted above, ~30 km south of La Selva) and local runoff (drainage from soil on hillslopes at La Selva) (Genereux and Pringle, 1994). The substantial chemical contrast between these two waters, with respect to both chloride and sodium concentrations, is the basis for the mixing calculations reported here.

3. Methods

Stream and spring samples were collected during April 27–29, 1994 throughout the two major drainage systems at La Selva (the Sura and Salto streams). Samples were taken from several minor streams as well as the Sura and Salto: the Pantano and Saltito (in the Salto basin), and the Taconazo and Arboleda (in the Sura basin). Elevations of the sampling sites ranged from about 35 to 120 m above sea level. Samples of water from a major spring just north of La Selva were also collected; this spring serves as a water supply for the town of Puerto Viejo de Sarapiqui, and the samples were taken from the tap at a home in Puerto Viejo (thus, the spring water samples represent untreated water that had traveled several km through PVC water supply pipe). Samples from the Salto basin (including the Salto, Saltito, and Pantano) were collected April 27 and 28 (both dry, sunny days); those from the Sura basin (Sura, Arboleda, and Taconazo) were collected April 29. All the sites in the Sura were sampled during the dry, sunny morning of the 29th, and seven sites were also sampled in the afternoon after a brief rain storm delivered 21 mm of precipitation. Samples were collected in 50 ml polyethylene bottles, and filtered through 0.45 μm membrane filters within a few hours of collection. Na and Cl concentrations of the water samples were measured by ion chromatography (Dionex DX-100) at the Drinking Water Research Center at Florida International University. High concentration samples were diluted to bring them into the linear calibration range.

4. Results

4.1. Concentrations and mixing proportions

Sodium and chloride data from streams at La Selva plot along a remarkably well-defined mixing line (Fig. 2), thus supporting the contention from earlier work that streamwater represents a mixture of two chemically distinct waters. The two samples falling in the upper right portion of Fig. 2, at the highest Na and Cl concentrations, are the samples from the large perennial spring. The cluster of samples in the lower left, at the lowest Na and Cl concentrations, includes eight samples collected from very small streams (a few centimeters deep, a few tens of centimeters wide) at relatively high elevation (except the Taconazo sampling point, which was at relatively low elevation). All the rest of the samples fall along a straight line which we interpret as a mixing line between geothermal groundwater (upper right of Fig. 2) and local runoff from rainfall on the hillslopes at La Selva (lower left of Fig. 2).

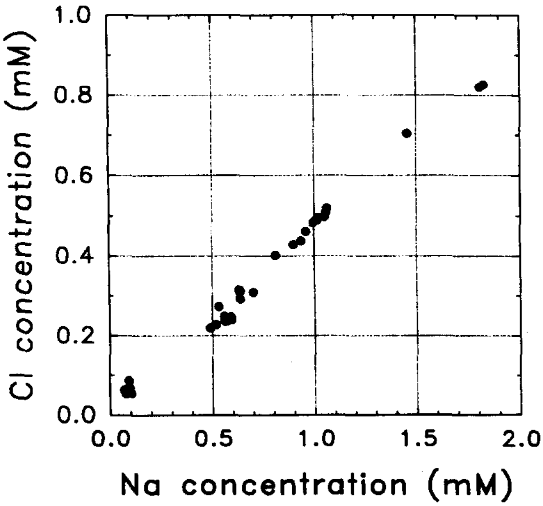

Fig. 2. Chloride content vs. sodium content for stream samples from La Selva. Eight samples plotting in the lower left define the chemistry of local runoff, while two samples in the upper right define geothermal groundwater. Other samples fall along a mixing line between these two components.

Eq. (1) was used to compute the fraction of flow at each sampling site due to geothermal groundwater, f_{gt} (Table 1). Calculations were made using both Na and Cl, so that at each site there is an f_{gt} value based on Na and an f_{gt} value based on Cl; differences between the results from the two solutes are discussed below. The overall pattern is the same from either Cl or Na, with streamwater f_{gt} values ranging from 0 to about 0.85, with the larger values further downstream and usually in the larger stream valleys. The f_{gt} values are probably at or near their annual maxima, since sampling was done at the end of the dry season, when local runoff would have been at its lowest.

These data and their interpretation have significant implications for water and chemical balances on watersheds in the area. For example, Cl data suggest that 57% of flow in the Salto (at the site farthest downstream, near the confluence with the Rio Puerto Viejo) was due to geothermal groundwater at the time of sampling (Na gave 54%). Stream discharge was also computed at this site, using current meter measurements in a stream cross-section of known dimensions (one measurement every 50 cm across the 2.5 m channel width). Total discharge was found to be 0.394 $m^3 s^{-1}$, or about 1.24×10^7 m^3 $year^{-1}$. Multiplying this discharge by the proportion of geothermal groundwater gives a yearly flux of 7.1×10^6 m^3 of geothermal groundwater from the Salto (this is most likely a minimum value, as it is reasonable to anticipate some seasonal fluctuation in this flux, with a minimum at or close to the end of the dry season). Averaged over the area of the Salto watershed, this flux corresponds to about 0.74 m of runoff per year. An interbasin transfer of this magnitude should be readily identifiable with accurate stream gauging, as the annual runoff expected in the absence of interbasin transfer is about 2.0 m (half the annual rainfall). Efforts are currently under way to establish permanent, high-quality stream gauging stations at the site.

The large interbasin transfer of geothermal groundwater represents an important consideration with regard to land use and the vulnerability of ecosystems (including human populations). It appears that a significant amount of rainfall in and near Braulio Carrillo National Park recharges groundwater that eventually discharges in lowland streams and springs. This relatively steady supply of high-solute, high-phosphorus water to streams and riparian zones has a significant effect on stream ecology, as discussed elsewhere (Pringle, 1990; Pringle et al., 1993; Pringle and Triska, 1991). Interruption of this water and solute supply could lead to significant changes in riparian ecosystems, possibly altering community structure and the rates of ecological processes such as primary production and organic matter decomposition. Changes in land use such as commercial timber harvesting in Braulio Carrillo could increase runoff and decrease recharge, leading to a decrease in the lowland discharge of geothermal groundwater. Besides affecting lowland riparian ecosystems and surface water quality, a decrease in groundwater recharge in Braulio Carrillo could adversely affect the water supply of the small city of Puerto Viejo de Sarapiqui, both by decreasing the flow of this large spring and possibly by increasing the solute concentrations in the remaining spring flow. Thus, in the presence of significant interbasin groundwater transfer over fairly long distances it is important to pursue land use and water resource planning with accurate knowledge of true "watershed" boundaries.

4.2. *Interbasin differences in solute behavior*

Cl, Na, and other major ions have often been used as "conservative" tracers in watershed-scale mixing models (see, for example, Hooper et al. (1990), Christophersen et al. (1990), Wels et al. (1991), Genereux et al. (1993) and Mulholland, 1993). While Cl and Na give the same overall picture of local runoff and geothermal groundwater mixing to form streamwater at La Selva, there are interbasin differences between f_{gt} values calculated with the two "conservative" solutes (Table 1). Na and Cl give very similar f_{gt} values for the eight low-solute samples that cluster in the lower left on Fig. 2 (Cl and Na give values that differ by 0.031, 0.017, and 0.013 for three samples, and values that differ by less than 0.01 for the other five samples). Other samples fall into two groups: those from the Sura, for which Na gave a higher f_{gt} (average difference of 0.037, standard deviation 0.013, for eleven samples), and those from other streams, for which Cl gave a higher f_{gt} (average difference of 0.023, standard deviation of 0.012, for seventeen samples).

Neither Cl or Na are truly conservative chemical tracers, and interaction with watershed soils could potentially alter aqueous concentrations of both. We expect such effects to be potentially more significant for Na, as the cation exchange capacity (CEC) for La Selva soils (average = 74 mmole of charge per kg of dry soil, standard deviation = 58, for 46 samples; Sollins et al., 1994) is significantly larger than the anion exchange capacity (AEC) (about 20 mmole kg^{-1}; Sollins, personal communication, August 19, 1994). Cl is weakly sorbed relative to oxyanions of Si, S, and P (Sollins et al., 1988), and its near-conservative behavior has made it a useful tracer in previous runoff studies (e.g., Eshleman et al., 1993).

With Cl behaving more conservatively than Na it would not be surprising to find f_{gt} values based on Cl slightly larger than those based on Na (as they are for high-solute samples from all streams but the Sura). This could result from geothermal groundwater

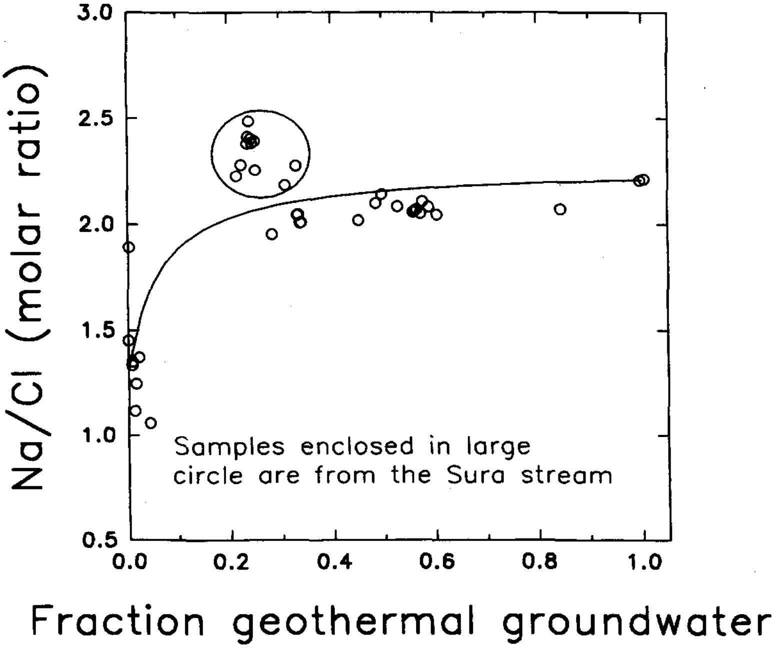

Fig. 3. Na/Cl (molar ratio) vs. fraction of sample accounted for by geothermal groundwater (f_{gt}) for stream samples from La Selva. The f_{gt} values are based on Cl. The solid line shows the theoretical curve along which mixtures of geothermal water and local runoff should fall, open circles show data. Eleven samples from the Sura cluster in the large circle above the curve, between f_{gt} values of 0.22 and 0.33. The solid curve was calculated using Na and Cl data from the samples taken to represent geothermal groundwater (large spring) and local runoff (the small stream with the lowest concentration); see text for discussion.

and/or mixtures of this water with local runoff losing some Na via sorption onto soils before the water reaches a stream. However, the Sura samples are unusual in this regard (and unique at La Selva), in that Na gave slightly higher f_{gt} values than Cl.

Differences between the Sura and other streams are not readily apparent on a traditional two-solute mixing plot (Fig. 2), but stand out clearly on a mixing plot of Na/Cl vs. f_{gt} (Fig. 3). Samples from streams other than the Sura closely track the theoretical mixing curve on Fig. 3. The bulk of the samples plot slightly below the theoretical mixing curve, suggesting that, averaged over the study basins, the geothermal groundwater component may actually have a slightly lower molar Na/Cl (around 2.1) than the two spring samples used to define the component in this study (Na/Cl = 2.2). However, all eleven samples from the Sura plot in a cluster above the theoretical mixing curve, at Na/Cl values between 2.2 and 2.5. This behavior could result from some combination of Na gain and/or Cl loss (or Na gain in excess of Cl gain) by water draining to the Sura.

None of the available soils data suggest significant watershed-wide differences in CEC, AEC, or other important geochemical parameters between the Sura and Salto basins. While the exact reason for the chemical differences between the Sura and Salto basins remains unknown, it seems that chemical ratio mixing plots like Fig. 3 can be useful for illustrating chemical differences among watersheds (e.g., the apparently non-conservative solute behavior at La Selva). Chemical differences between the Sura and other streams are immediately obvious on Fig. 3, but are not apparent on the two-solute mixing diagram (Fig. 2), the standard style of plot commonly used in streamflow generation studies with natural tracers.

5. Summary

At La Selva Biological Station, there appear to be two chemically and hydrologically distinct waters which contribute to streamflow and which can serve as components or end-members in a mixing model: low-solute local runoff and high-solute geothermal groundwater. Interpretation of streamwater Na and Cl data in the framework of this mixing model suggests the occurrence of large subsurface interbasin transfers of geothermal water and solutes (about 33% of flow in the Sura and 57% of flow in the Salto, the two major streams at La Selva, were due to geothermal groundwater at the end of the dry season in 1994). This has significant implications for quantification of hydrologic and geochemical budgets on this landscape, as well as water resource and land use planning. Determination of a water budget for one of the study basins using only measurements of streamflow and precipitation (and calculating ET by difference) would lead to an erroneously low value of ET. The errors would only be detected if there were reliable independent measurements of ET, or chemical data as presented here and in previous studies (Pringle, 1991; Pringle et al., 1993). Conversely, an accurate hydrologic budget would provide a strong check on our interpretation of existing chemical data. Obtaining the required information for compilation of hydrologic budgets is a major goal of future work at La Selva.

Both Na and Cl offer the same general picture of the spatial distribution of mixing between geothermal groundwater and local runoff in the streams at La Selva, though there remain some questions concerning the consistent differences in solute trends between the Sura and Salto watersheds. Solute ratio mixing diagrams such as Fig. 3 may be a sensitive tool for detecting non-conservative solute behavior and hydrogeochemical differences between watersheds (differences overlooked on traditional two-solute mixing plots such as Fig. 2).

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