Chemical and isotopic signature of old groundwater and magmatic solutes in a Costa Rican rain forest: Evidence from carbon, helium, and chlorine

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[1] C, He, and Cl concentrations and isotopes in groundwater and surface water in a lowland Costa Rican rain forest are consistent with the mixing of two distinct groundwaters: (1) high-solute bedrock groundwater representing interbasin groundwater flow (IGF) into the rain forest and (2) low-solute local groundwater recharged in the lowlands. In bedrock groundwater, high $\delta^{13}C$ (−4.89‰), low ^{14}C (7.98 pM), high R/R_A for He (6.88), and low $^{36}Cl/Cl$ (17×10^{-15}) suggest that elevated tracer concentrations are derived from magmatic outgassing and/or weathering of volcanic rock beneath nearby Volcan Barva. In local groundwater, the magmatic signature is absent, and data suggest atmospheric sources for He and Cl and a biogenic soil gas CO_2 source for dissolved inorganic carbon. Dating of ^{14}C suggests that the age of bedrock groundwater is 2400–4000 years (most likely at the lower end of the range). Local groundwater has $^{14}C > 100$ pM, indicating the presence of "bomb carbon" and thus ages less than ∼55 years. Overall, data are consistent with a conceptual hydrologic model originally proposed on the basis of water budget and major ion data: (1) large variation in solute concentrations can be explained by mixing of the two distinct groundwaters, (2) bedrock groundwater is much older than local groundwater, (3) elevated solute concentrations in bedrock groundwater are derived from volcanic fluids and/or rock, and (4) local groundwater has not interacted with volcanic rock. Tracers with different capabilities converge on the same hydrologic interpretation. Also, transport of magmatic CO_2 into the lowland rain forest via IGF seems to be significant relative to other large ecosystem-level carbon fluxes.

1. Introduction

[2] Interbasin groundwater flow (IGF), groundwater flow beneath the surface topographic divides of watersheds, is a basic groundwater process [*Tóth*, 1963] that may be an important influence on the quantity and quality of water in the watersheds involved. In addition to its significance for water balance, chemical transport, and water resource planning, IGF may be linked to climate [*Schaller and Fan*, 2009] and play a role in the persistence of multiyear precipitation anomalies [*Bierkens and van den Hurk*, 2007].

[3] Previous work suggests IGF is an important control on hydrology and water quality in a lowland rain forest in Costa Rica [*Genereux et al.*, 2005; *Genereux and Jordan*, 2006]. The conceptual hydrologic model for the site is that it represents a complex lowland discharge area where two distinct groundwaters mix and discharge to streams and wetlands: deep regional bedrock groundwater recharged in the Cordillera Central (and representing IGF into the lowland watersheds), and younger locally recharged groundwater. In these watersheds IGF increases stream discharge (up to several m/a), major ion concentrations and export in streams (accounting for 90–99%), and soluble reactive phosphorus concentrations (up to 300 ppb), and helps maintain riparian swamps (accounting for over 80% of the water in some) [*Pringle et al.*, 1990; *Genereux et al.*, 2002, 2005].

[4] These findings are based mainly on physical hydrologic data (annual water budgets for watersheds) and major ion data, with additional support from ^{18}O and phosphorus data. Prior to the work reported here and in a companion paper (D. K. Solomon et al., Testing mixing models of old and young groundwater in a tropical lowland rainforest with environmental tracers, submitted to *Water Resources Research*, 2009), there had been no application of advanced isotopic, trace gas, or age-dating tracer methods at the site, though earlier results suggest clear hypotheses that could be tested with such tracers (e.g., that the high-solute groundwater involved in IGF is older than the low-solute ground-

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water, and that the two groundwaters have different solute sources and recharge elevations).

[5] The work presented here and the work by Solomon et al. (submitted manuscript, 2009) addresses these hypotheses, while evaluating both (1) the conceptual hydrologic model (centered on IGF and mixing of two distinct groundwaters) and (2) the consistency among tracers with different source functions, behaviors, and abilities in elucidating the hydrology at a site that seems to have extensive mixing between hydrogeochemically distinct groundwaters. This paper focuses on carbon, helium, and chlorine isotopes ($\delta^{13}C$, ^{14}C, $^3He/^4He$, and $^{36}Cl/Cl$) and concentrations in groundwater and surface water; Solomon et al. (submitted manuscript, 2009) report results for trace gases (noble gases, CFCs, and SF_6) and tritium.

[6] These tracers have been used in a number of previous groundwater studies, but are usually not all applied together. Most studies focus on a groundwater system with either relatively young groundwater (decades old) or old groundwater (thousands of years old), and choose a tracer or group of tracers accordingly: usually CFCs, SF_6, and/or $^3H/^3He$ dating for studies of young groundwater [e.g., *Plummer et al.*, 2001; *Cook et al.*, 2003; *Tesoriero et al.*, 2005; *Koh et al.*, 2006] and C isotopes or ^{36}Cl in studies of old groundwater [e.g., *Phillips et al.*, 1986; *Torgersen et al.*, 1991; *Clark et al.*, 1998; *Plummer and Sprinkle*, 2001; *Aeschbach-Hertig et al.*, 2002; *Zuber et al.*, 2004], with noble gases used in both groups of studies but the full suite of noble gases being more common in studies of old groundwater. Tracers appropriate for both young and old groundwater were used in the work reported here and in the work by Solomon et al. (submitted manuscript, 2009), to test the conceptual model concerning mixing of young and old groundwaters at the study site.

2. Study Site

[7] The study site, the area in and near La Selva Biological Station (LSBS) in Costa Rica, has previously been described in detail [*Pringle et al.*, 1993; *Genereux et al.*, 2002, 2005; *Genereux and Jordan*, 2006; *Webb*, 2007]. It lies at the foot of Volcan Barva (elevation 2906 m), between the steep foothills of this large composite volcano and the Caribbean coastal plain. LSBS (Figures 1 and 2) is a 1536-ha research and education preserve that forms the downslope end of a tract of primary rain forest extending over 30 km to the south (Figure 1), through Braulio Carrillo National Park on the north slope of Volcan Barva. Other large peaks in the region include Irazú, Poás, and Arenal (about 32 km southeast, and 15 and 75 km northwest, respectively, of Barva).

[8] Geology of the area consists of Quaternary volcanic rocks (mainly andesitic to basaltic lavas, ignimbrites, volcanic tuffs and breccias), with interbedded mudflow deposits, ash, and paleosols [*Bourgeois et al.*, 1972; *Castillo-Muñoz*, 1983; *Foster et al.*, 1985; *Parker et al.*, 1988; *Alvarado-Induni*, 1990]. On the south flank of Barva, lavas generally function as aquifers and ignimbrite beds as aquitards [*Parker et al.*, 1988]. Much of the discharge from lavas is via significant springs with relatively steady year-round flow [*Parker et al.*, 1988]; one such spring (Guacimo Spring, Figure 1) represents our best sampling point for the
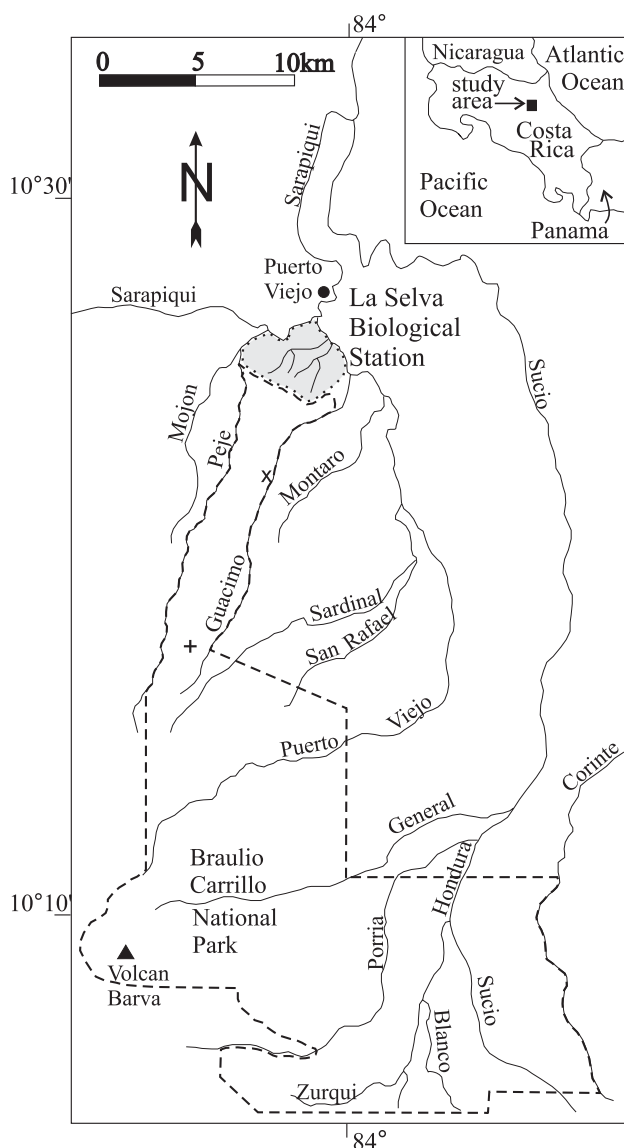

Figure 1. Location of La Selva Biological Station (LSBS, the shaded area within the dotted line) and surrounding area in Costa Rica. The two streams shown within LSBS are the Sura (to the west) and Salto. LSBS sits at the northern end of Braulio Carrillo National Park; the dashed line shows the park boundary. Two sampling sites outside LSBS are shown (Guacimo Spring, marked with a cross on the left bank of the Guacimo River, and BCNP1, marked with a plus farther upslope from LSBS).

bedrock groundwater in the conceptual hydrologic model mentioned in section 1.

[9] Most of what is known about the geology is based on work from the south side of Volcan Barva, toward the populous Central Valley and capital city of San Jose. Similar geology is expected on the north side of Barva (toward our study site), though lack of access to the dense nearly roadless national park jungle on the north side has not allowed for the scientific core boring and hydrogeologic data collection often done in more developed areas. Without access to the regional groundwater of the Cordillera over the full distance from peaks to lowlands, the field sampling in
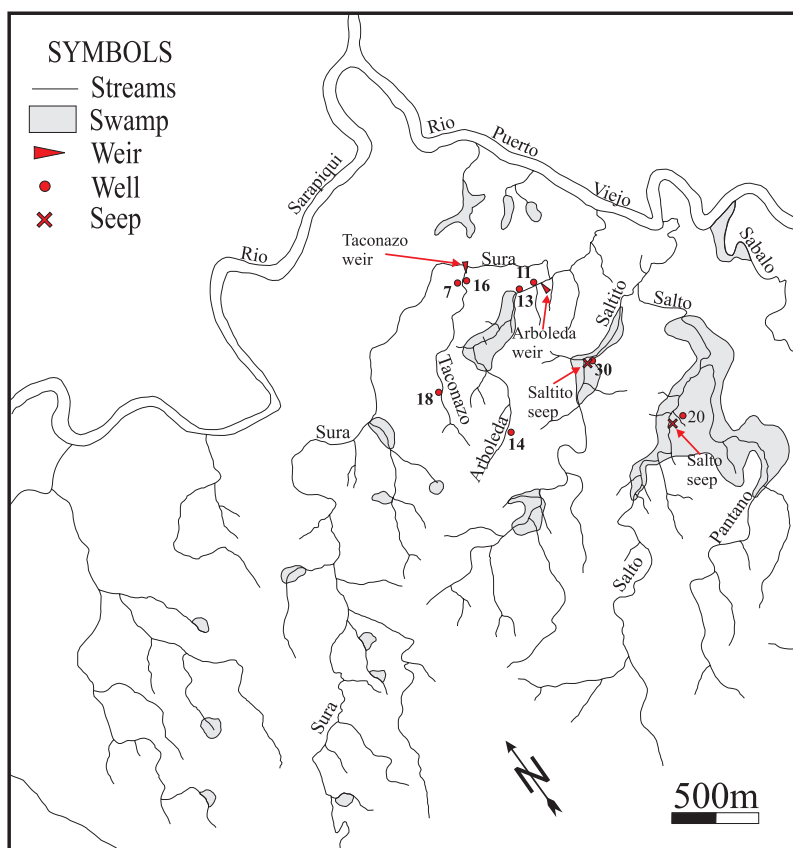
Figure 2. Streams and sampling sites at La Selva Biological Station. Two sampling sites (Guacimo Spring and BCNP1) are outside LSBS and the area of the map (see Figure 1).

this and previous studies focuses on the effects of this groundwater in the lowland discharge area in and around LSBS.

[10] The major soil orders at LSBS are Ultisols (45% of area; mainly Typic Tropohumults) and Inceptisols (55% of area; various suborders) [*Sollins et al.*, 1994]. Inceptisols are found in the valley bottoms and on the alluvium occupying the northern portion of the research station, Ultisols in other areas. Small areas of Entisols (<0.5% of land area) are found near the Rio Sarapiqui. On most ridges a thick clayey saprolite several meters thick lies between the overlying soil (roughly a meter in thickness) and underlying bedrock.

[11] Average annual temperature at LSBS is 25.8°C [*Sanford et al.*, 1994]. Annual precipitation averaged 4240 mm during the years 1958–2002 (Organization for Tropical Studies, Meteorological data for La Selva Biological Station, 2004, http://www.ots.duke.edu/en/laselva/metereological.shtml). February, March, and April are the driest months, averaging about 180 mm per month. Annually, ET is about half or slightly more of precipitation [*Loescher et al.*, 2005]. The Sura and Salto are the major streams within LSBS (Figure 2).

[12] *Genereux and Jordan* [2006] review prior work related to IGF at LSBS. The $\delta^{18}O$ data and major ion data are consistent with the presence and mixing of two distinct groundwaters: (1) local groundwater, a low-solute water draining from hillslope soils after little or no contact with bedrock, and sampled from the Taconazo (Figure 2) and other small streams, and from shallow wells, at elevations above 50 m, and (2) bedrock groundwater, a high-solute water sampled from Guacimo Spring (Figure 1) and thought to represent discharge from a regional groundwater system that is recharged south of LSBS at high elevation in the Cordillera Central.

[13] Linear trends on two-solute plots (e.g., Na^+ concentration versus Cl^- concentration) suggest that most of the variability in major ion concentrations in surface water and groundwater at LSBS can be explained by mixing between the two groundwaters [*Genereux and Pringle*, 1997; *Genereux et al.*, 2002]. Mean concentrations for major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, and SO_4^{2-}) in bedrock groundwater range from 13 (for Cl^-) to 29 (for Mg^{2+}) times larger than the corresponding means in local groundwater. Mixing calculations based on Cl^- concentrations suggest that bedrock groundwater accounts for about 25–50% of water in the Salto, Sura, and Arboleda streams (Figure 2), none of the stream water in the Taconazo, and 0–84% of groundwater in riparian zones [*Genereux et al.*, 2002].

[14] A number of lines of evidence and reasoning strongly suggest that bedrock groundwater represents IGF into the lowland rain forest in and around LSBS. Annual water budgets show that stream discharge from the Arboleda watershed includes >4 m/a of bedrock groundwater (in addition to a large discharge of low-solute local water), a quantity of water too large to be explained by local

Table 1. Sampling Sites[a]

Site	Type	Installed	Screened Interval (cm)	Stick Up (cm)	Water Level (cm)
Well 7	PVC well	Feb 2000	71–116.5	28	92, 64
Well 11	PVC well	Feb 2006	176.5–207.5	14	82.5, 72
Well 13	PVC well	Nov 2005	103.5–134.5	26	103, 82
Well 14	PVC well	Nov 2005	77.5–108.5	52	35
Well 16	PVC well	Feb 2006	155.5–186.5	35	87
Well 18	PVC well	Mar 2006	94.5–125.5	35	34
Well 20	PVC well	Nov 2005	87.5–118.5	42	86.5
Well 30	PVC well	Feb 2006	76.5–107.5	53	32
Salto seep	GW seep	NA	NA	NA	NA
Saltito seep	GW seep	NA	NA	NA	NA
Arbo weir	stream weir	Jun 1998	NA	NA	NA
Taco weir	stream weir	Jun 1998	NA	NA	NA
Guacimo S.	concrete cistern	pre-1998	NA	NA	NA
BCNP1	GW seep	NA	NA	NA	NA

[a]NA, not applicable; GW, groundwater. Screened intervals and water levels are in cm below ground surface. Water levels were measured before the start of sampling in March 2006 (where two values appear, the second was measured before sampling in December 2006). Stick Up is the length of casing above ground surface.

precipitation onto the watershed, while the adjacent Taconazo watershed has only local water and its water budget is in balance, within experimental error, without IGF [*Genereux et al.*, 2005]. With regard to $\delta^{18}O$, bedrock groundwater is both isotopically lighter and less variable over time than local water [*Genereux*, 2004], consistent with bedrock groundwater being recharged at an elevation several hundred meters above LSBS and discharged after relatively long transit through a large groundwater system (both are consistent with IGF).

[15] The conceptual hydrologic model outlined above suggests that bedrock groundwater should be both much older than low-solute local groundwater (perhaps thousands of years versus a few decades) and recharged at a higher elevation (this is the driving force for IGF). Also, bedrock groundwater should have a different dominant solute source (its high solute load must be acquired through subsurface processes not experienced by local groundwater). Here and in the work by Solomon et al. (submitted manuscript, 2009), we test these hypotheses with naturally occurring and anthropogenic age dating, trace gas, and isotopic tracers. We will use the terms "local water" and "local groundwater" to indicate the same water but to distinguish between points or conclusions that apply to all occurrences of such water (local water, in streams and in the subsurface) and those that apply only to the subsurface (local groundwater, which may have dissolved gas characteristics that differ from those of local water in streams).

3. Methods

[16] Water samples were collected at 14 different sites (Figure 2 and Table 1); 13 sites were sampled during the dry season, in March 2006, and 4 of those plus one additional site were sampled during the wet season, in December 2006 (Table 2). The sites were 3 wells in the Arboleda watershed, 3 wells in the Taconazo watershed, stream water at a weir in each watershed, one well and one small groundwater seep in riparian swamp near each of the Salto and Saltito streams, Guacimo Spring, and a groundwater seep upslope from LSBS on Volcan Barva at an elevation (about 660 m) previously suggested as a potential recharge area for bedrock groundwater [*Genereux*, 2004]. Details of the special-ized sampling and analytical methods can be found in the auxiliary material.[1]

4. Results and Discussion

4.1. Presence and Mixing of Two Distinct Groundwaters

[17] Data from the 14 sampling sites show a wide range of C, He, and Cl concentrations and isotopic values (Table 2). Comparing between the site with the highest solute concentrations (Guacimo Spring) and those with the lowest (wells 7, 14, 16, 18, Taco weir, and BCNP1), [DIC] (the concentration of dissolved inorganic carbon) ranged from 13.9 to about 0.26 mM, the $\delta^{13}C$ and ^{14}C of DIC ranged from −4.89 ‰ and 7.98 pM (pM = percent modern [*Plummer et al.*, 2004, p. 38]) to −26.4 ‰ and 117 pM, [^{4}He] (nearly identical to total [He]) ranged from 734 to 44 pL of gas at standard temperature and pressure per gram of water, R/R$_A$ (^{3}He/^{4}He of the sample divided by ^{3}He/^{4}He of the atmosphere) ranged from 6.88 to 0.97, and [Cl] ranged from 0.91 to 0.06 mM. ^{36}Cl/Cl was highly variable among samples of low [Cl]: $7-228 \times 10^{-15}$ (a factor of 33 between high and low, even without the highly uncertain outlier of well 30), but was consistently low among samples of higher [Cl] ($10-26 \times 10^{-15}$). Poisoning samples with HgCl$_2$ had no significant effect on the ^{14}C and δ^{13}C of DIC (Table 3).

[18] In cases in which two waters mix, and an element is present at different concentrations and with different isotopic abundances in the two waters, mixtures are expected to show a linear relationship between the measure of isotopic abundance and the inverse of concentration [e.g., *Faure*, 1977, p. 98–101]. For C, He, and Cl, we found highly significant linear trends (p values all ≪0.05) on plots of isotopic abundance versus the inverse of concentration (Figures 3, 4, and 5), strongly supporting the conceptual model of mixing between bedrock groundwater and local water. Bedrock groundwater is low in ^{14}C and ^{36}Cl/Cl, and high in [DIC], δ^{13}C, [He], [Cl], and R/R$_A$; local water is opposite in every respect, with the exception that it may be

Table 2. Geochemical Data[a]

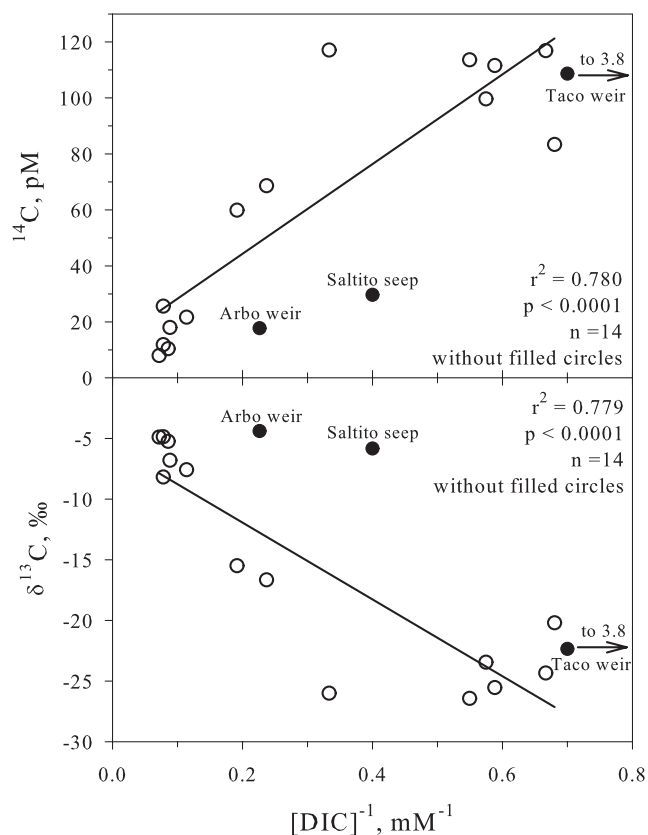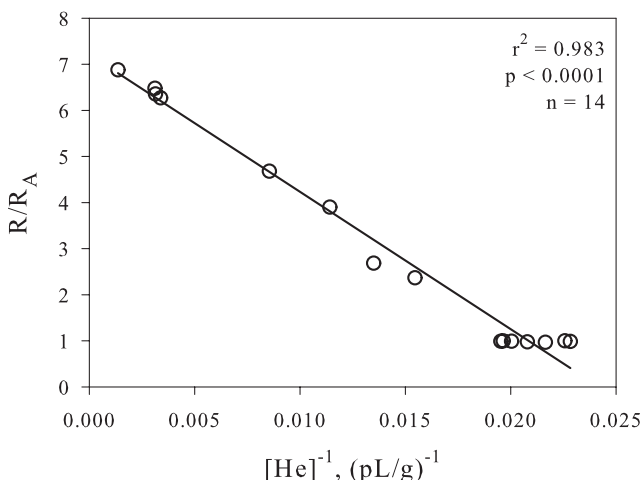| Site	T (deg C)	pH	Alk (mN)	Na (mM)	K (mM)	Mg (mM)	Ca (mM)	SO₄ (mM)	Cl (mM)	DIC[b] (mM)	DOC (mM)	$\delta^{13}C$ (‰)[c]	^{14}C (pM)[c]	$^{36}Cl/Cl \times 10^{15}$	^4He (pL/g)[d]	R/R_A	CFC-12 (pmol/kg)[e]
March 2006 Samples																	
Well 7	24.7	4.45	<0.002	0.061	<0.003	0.011	0.011	0.005	0.059	<3	0.20	−26.00	117.1	228	48.1	0.978	1.664
Well 11	25.4	5.98	2.6	1.02	0.090	0.658	0.599	0.084	0.463	8.76	<0.08	−7.58	21.7	24	295	6.270	0.138
Well 13	24.9	5.93	1.4	0.400	0.021	0.370	0.339	0.023	0.203	5.23	0.13	−15.49	59.9	27	117	4.679	1.032
Well 14	24.9	4.85	0.038	0.113	<0.003	0.010	0.025	0.012	0.065	1.70	0.20	−25.54	111.6	10	46.2	0.968	1.712
Well 16	25.0	4.61	<0.002	0.042	<0.003	0.011	0.025	0.013	0.051	<1.5	<0.08	−24.34	116.9	112	49.9	0.991	1.621
Well 18	24.8	5.18	0.10	0.257	<0.003	0.006	0.052	0.058	0.059	1.75	0.08	−23.45	99.7	7	51.2	0.990	1.690
Well 20	25.3	NA	3.8	1.64	0.151	1.06	0.544	0.087	0.666	11.32	<0.08	−6.80	18.0	17	NA	NA	0.829
Well 30	24.8	5.78	0.31	0.213	0.017	0.086	0.100	0.071	0.084	1.47	0.32	−20.20	83.4	590	74.1	2.685	1.448
Salto seep	25.7	6.05	3.9	1.46	0.184	1.17	0.646	0.080	0.728	11.68	<0.08	−5.24	10.4	13	NA	NA	0.166
Saltito seep	25.1	6.50	1.5	0.574	0.061	0.387	0.254	0.025	0.299	2.51	0.42	−5.83	29.7	69	64.7	2.367	1.172
Arbo weir	26.3	6.43	2.4	0.931	0.115	0.662	0.467	0.041	0.429	4.41	0.08	−4.39	17.7	26	NA	NA	1.023
Taco weir	24.7	5.63	0.040	0.070	0.008	0.015	0.016	0.004	0.062	0.26	0.39	−22.35	108.7	160	44.3	0.999	1.560
Guacimo S.	25.8	6.13	5.2	1.95	0.240	1.60	0.781	0.144	0.914	13.92	<0.08	−4.89	7.98	17	734	6.880	0.0781
December 2006 Samples																	
Well 7	24.9	3.40[f]	0.05	0.052	0.019	0.011	0.011	0.004	0.054	NA	0.14	−26.2	115.1	220	50.9	0.998	1.68
Well 11	25.3	5.69	2.3	0.85	0.084	0.63	0.49	0.030	0.38	12.8	0.07	−8.18	25.6	11.4	318	6.355	0.16
Well 13	25.5	5.95	1.2	0.35	0.012	0.32	0.28	0.016	0.14	4.22	0.03	−16.7	68.6	27.6	87.6	3.937	0.86
Salto seep	25.0	5.97	3.8	1.42	0.18	1.18	0.66	0.079	0.76	12.8	<0.01	−4.86	11.9	9.5	321	6.478	0.38
BCNP1	22.4	4.70	0.02	0.038	0.016	0.010	0.004	0.004	0.055	1.82	0.04	−26.4	113.6	112	43.8	0.987	1.65

    [a]NA, not available.

    [b]Calculated from pH and Alk.

    [c]The $\delta^{13}C$ and ^{14}C of DIC. March 2006 data are for samples poisoned with HgCl₂; December 2006 samples were not poisoned (see Table 3). Following _Plummer et al._ [2004, p. 38], pM is percent modern normalized for ^{13}C isotopic fractionation (above), and pmC is percent modern carbon not normalized for ^{13}C isotopic fractionation (Table 4) (used in age-dating calculations).

    [d]Picoliters of ^4He gas, at STP, per gram of water; for wells 7 and 18, number is an average based on one copper tube (CT) sample and two diffusion samplers (DS); for well 16, number is an average based on two DS; coefficients of variation for ^4He content and R/R_A were 0.7% for well 7, 0.8% and 0.3% for well 7 and 18, number is an average based on two DS; 2006) are based on a single DS; all other sites are based on a single CT.

    [e]Picomoles of CFC-12 per kilogram of water.

    [f]Value is about 1 pH unit lower than the March 2006 values from this well and similar wells; may be erroneous.

Table 3. The ^{14}C and $\delta^{13}C$ of DIC in Poisoned and Unpoisoned Samples Collected in March 2006

Site	$\delta^{13}C$ (‰)		^{14}C (pM)	
	Poisoned	Unpoisoned	Poisoned	Unpoisoned
Well 11	−7.58	−7.62	21.7	21.8
Well 16	−24.34	−24.44	116.9	116.7
Guacimo Spring	−4.89	−4.89	7.98	7.96

either high or low in $^{36}Cl/Cl$ (a phenomenon discussed below).

[19] Scatter in the carbon plots (Figure 3) is associated with DIC in two ways. First, three surface water samples (Arbo weir, Taco weir, and Saltito seep) seem to have been affected by loss of CO_2 (shifting them to the right in Figure 3), as expected for groundwater discharged into small streams and seeps. BCNP1 and Salto seep were not similarly affected, most likely because they were sampled from larger deeper pools that continually overflowed from stronger groundwater discharge, providing relatively little opportunity for gas exchange prior to sampling. Arbo weir, Taco weir, and Saltito seep were excluded from the regressions in Figure 3 because of the obvious potential for gas exchange to cause them to deviate from the mixing trend. Second, the low values of [DIC] have a large relative uncertainty (arising from the large relative uncertainty in

Figure 4. R/R_A for dissolved He versus the inverse of [He].

the low values of Alk, from which [DIC] was calculated). For example, well 7 falls below the mixing trend at $[DIC]^{-1} = 0.33$ mM^{-1} in Figure 3, but this value is a lower limit (given [DIC] < 3 mM, Table 1) and could easily be 0.6 or 0.7 (if [DIC] were about 1.5 mM).

[20] When $[Cl]^{-1}$ (which is not affected by gas exchange) is substituted for $[DIC]^{-1}$ in the carbon plots, the three surface water samples affected by CO_2 loss fall along the same trend as the others (Figure 6). [Cl] is closely correlated with [DIC] ($r^2 = 0.88$, p < 0.0001, n = 14 without Arbo, Taco, and Saltito seep) and is probably the simplest and most conservative index of mixing between bedrock groundwater and local water. It has been used extensively in this role [*Genereux and Pringle*, 1997; *Genereux et al.*, 2002, 2005; *Genereux and Jordan*, 2006]. The data in Figures 3–6 strongly support the hypothesis of mixing between bedrock groundwater and local water, and together show that water samples may deviate from the mixing trend

Figure 3. Values of ^{14}C and $\delta^{13}C$ versus the inverse of [DIC]. The three surface water samples indicated by solid circles were excluded from the linear regressions. The sample from Taco weir plots out of the range of the graph (at $[DIC]^{-1} = 3.8$).
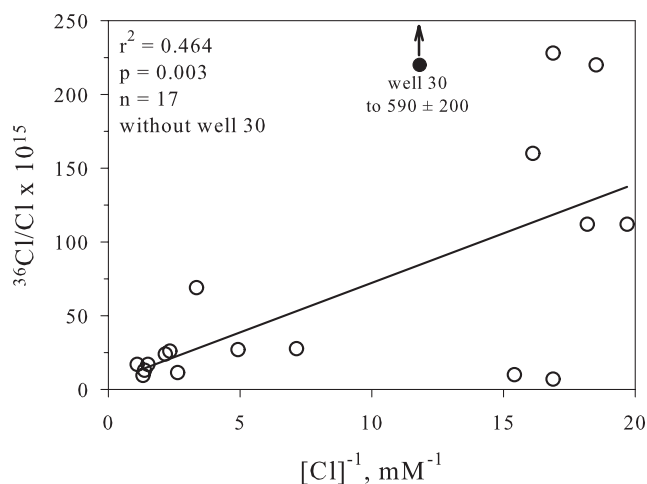
Figure 5. Values of $^{36}Cl/Cl$ (measured values were multiplied by 10^{15} for plotting) versus the inverse of [Cl]. The sample from well 30 plots out of the range of the graph (at $^{36}Cl/Cl \times 10^{15} = 590$) and was not included in the linear regression.
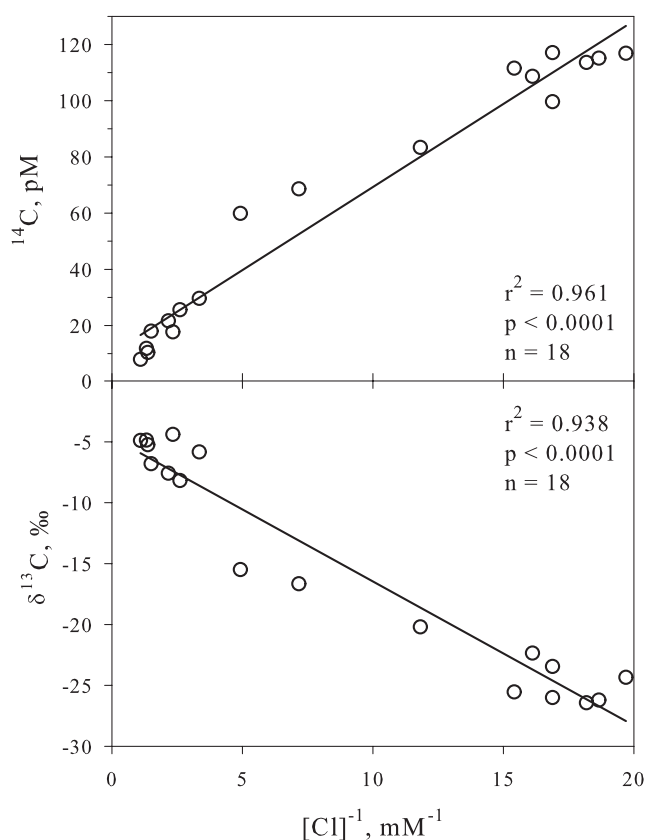
Figure 6. Values of ^{14}C and $\delta^{13}C$ versus the inverse of [Cl].

following the loss of CO_2 in stream channels or surface rivulets from seeps. Loss of dissolved He from water to air at the three sites discussed above does not affect the linear trend in Figure 4 because Arbo is not shown in Figure 4 (we do not have He data from this site), Taco plots in the lower right along with the low-solute groundwater samples (e.g., local water has the same dissolved He characteristics, whether in a stream or in the subsurface), and at Saltito seep any He loss or equilibration with the atmosphere apparently occurred such that decreases in both R/R_A and [He] kept the sample near the mixing trend. Beyond mixing, the data offer additional insights into solute sources and, in the case of bedrock groundwater, age.

4.2. Solute Sources in Local Water

[21] The ^{14}C, $\delta^{13}C$, and [DIC] in local water (wells 7, 14, 16, and 18, Taco weir, and BCNP1) is consistent with expectations for young shallow groundwater in an area without limestone or dolomite. A value of $^{14}C > 100$ pM indicates the presence of bomb carbon and therefore water recharged since the 1950s [Kalin, 2000]. The $\delta^{13}C$ is consistent with expectations for biogenic CO_2 in soil, in general [Galimov, 1966; Cerling et al., 1991; Amundson et al., 1998; Geyh, 2000] and at La Selva in particular (-23 to -25 ‰) [Schwendenmann and Veldkamp, 2006]. With no solid carbonate in the shallow (<1 km) subsurface at La Selva, the $\delta^{13}C$ of DIC in shallow groundwater is expected to be essentially that of biogenic soil CO_2.

[22] Dissolved He concentrations of about 50 pL (at STP) per gram of water and R/R_A values of about 1 at these six

sites are consistent with the dominant He source being dissolution of atmospheric He into recharge water [Solomon and Cook, 2000]. Obviously stream water at Taco weir had the opportunity to at least partially reequilibrate with the atmosphere, but even groundwater in the Taconazo watershed (wells 7, 16, and 18) is in equilibrium with the atmosphere with respect to [He] and R/R_A.

[23] The variation of $^{36}Cl/Cl$ in the low-solute local waters ($7-228 \times 10^{-15}$) is similar to that found in precipitation in Maryland, USA ($4-568 \times 10^{-15}$) [Hainsworth et al., 1994] and Seville, Spain ($4-300 \times 10^{-15}$) [Santos et al., 2004]. Also, the mean [Cl] in this water (0.06 mM) is only slightly higher than the mean [Cl] in precipitation at La Selva (0.048 mM) [Eklund et al., 1997]. These two observations are consistent with local water being relatively young and having no subsurface source of Cl.

[24] Temporal variation in the $^{36}Cl/Cl$ of atmospheric deposition (which we did not measure) may be at least partly responsible for the observed spatial variation in the $^{36}Cl/Cl$ of local water. Temporal variability in the $^{36}Cl/Cl$ of precipitation can arise from variations in troposphere-stratosphere mixing, on seasonal or shorter time scales [Suter et al., 1987; Hainsworth et al., 1994; Knies et al., 1994; Santos et al., 2004]. Also, the presence of marine "sea salt" Cl with very low $^{36}Cl/Cl$ ($<10^{-15}$) [Rao et al., 1996] is an important factor in producing low $^{36}Cl/Cl$ values in precipitation [Hainsworth et al., 1994; Santos et al., 2004]. Eklund et al. [1997] concluded that over 90% of Cl in atmospheric deposition at LSBS was derived from sea salt and that the sea salt contribution was variable on seasonal and shorter time scales, observations that would suggest significant temporal variation in the $^{36}Cl/Cl$ of atmospheric deposition at LSBS. Also, at LSBS and other active volcanic regions, time-varying volcanic emissions may influence the amount of Cl in atmospheric deposition [e.g., Veneklaas, 1990; Genereux et al., 2005] and thereby possibly the $^{36}Cl/Cl$ of atmospheric deposition. In a companion paper we show that the local water samples with low [Cl] and variable $^{36}Cl/Cl$ ranged in age from about <1 to 8 years at the time of collection in 2006; these samples thus contain groundwater recharged at different periods of time with precipitation having potentially different $^{36}Cl/Cl$ for reasons discussed above. It seems likely that the wide range of $^{36}Cl/Cl$ in low-solute local water is the product of atmospheric processes that produce temporal variability in the $^{36}Cl/Cl$ of atmospheric deposition (rather than subsurface hydrogeochemical processes).

[25] Thus, concentrations and isotopic ratios of C, He, and Cl in low-solute local water are consistent with atmospheric/precipitation sources for He and Cl and a biogenic soil gas CO_2 source for DIC. If these local water samples are representative of recharge to the bedrock groundwater system, concentrations in the two types of water (Table 2) suggest that bedrock groundwater acquires at least 90% of its dissolved C, He, and Cl in the subsurface, after recharge and before discharge to surface water at and near LSBS. The isotopic data place strong constraints on the likely source of those added solutes.

4.3. Solute Sources in Bedrock Groundwater

[26] Figure 7 suggests that if the subsurface source of DIC to bedrock groundwater had no ^{14}C its $\delta^{13}C$ would be
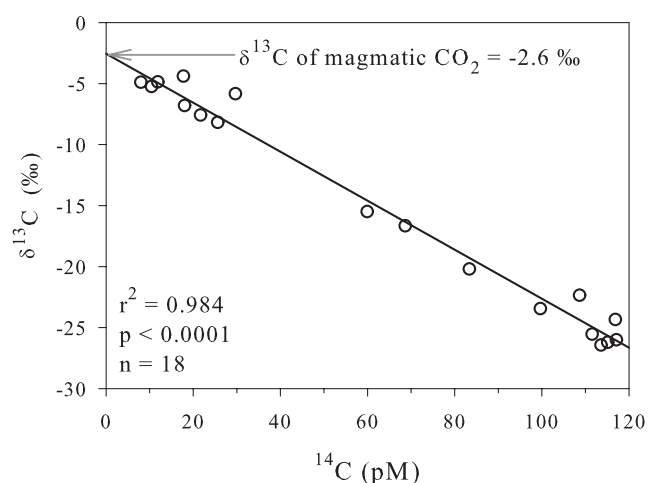
Figure 7. Values of $\delta^{13}C$ versus ^{14}C. The intercept at $^{14}C = 0$ provides an estimate of the $\delta^{13}C$ of magmatic CO_2 ($-2.6‰$).

about -2.6 ‰. This value is somewhat light for marine limestones, with average $\delta^{13}C$ of about 0 ‰ [Keith and Weber, 1964; Faure, 1977]. Also, the physical geological setting and other aspects of groundwater chemistry at Guacimo Spring argue against marine limestone as the source of elevated DIC in bedrock groundwater. Geologic information from the area is a bit sparse but suggests the shallowest limestones are probably too deep [Weyl, 1980] to be encountered by groundwater flow paths moving downslope on Volcan Barva. Groundwater flow on the south side of Barva typically follows lava flows [Parker et al., 1988], and it is reasonable to expect the same on north side of Barva, toward LSBS. Also, values of [DIC], pH, and [Ca] for groundwater in carbonate rocks are typically $\leq$ 6 mM, 7–9, and 1–3 mM, respectively [e.g., Freeze and Cherry, 1979, p. 263; Plummer and Sprinkle, 2001; McIntosh and Walter, 2006]. The values measured at Gaucimo Spring (13.9 mM, 6.1, and 0.78 mM, respectively) are more consistent with dissolution of CO_2 into groundwater (leading to high [DIC] with relatively low pH and [Ca]) than dissolution of solid carbonate. Magmatic CO_2 beneath Volcan Barva and nearby areas of the Cordillera Central is a potential source of such CO_2.

[27] Diffuse magmatic degassing occurs through the lower flanks of nearby Volcan Poás and Volcan Arenal, on the basis of Rn, pCO_2, and $\delta^{13}C$ data from soil gas [Williams-Jones et al., 2000]. Degassing of CO_2 through the flanks of volcanoes has also been described in a number of other studies [Notsu et al., 2005, and references therein]. High concentrations of DIC of magmatic origin have been found in groundwater in the United States [Rose and Davisson, 1996; James et al., 1999; Evans et al., 2002], Italy [Allard et al., 1997; Chiodini et al., 2000], Japan [Ohsawa et al., 2002], and Cameroon [Tanyileke et al., 1996]; most of these studies discuss and/or quantify the relative contributions to groundwater DIC from biogenic CO_2 and magmatic CO_2.

[28] Carbon isotopes have been important tools in this work, given the large isotopic contrast between biogenic and magmatic CO_2. Biogenic CO_2 is generally in the range

-22 to -26 ‰ for $\delta^{13}C$, and >100 pM for ^{14}C. Magmatic CO_2 has essentially zero pM, and $\delta^{13}C$ varies from about -2.5 to -8 ‰ in most subduction zones [Javoy et al., 1986; Fischer et al., 1997], with rare exceptions such as the heavier values (average about 1.5 ‰) from the Izu-Ogasawara arc, Japan [Sumino et al., 2004] and lighter values from Mount St. Helens, United States (down to -11.5 ‰) [Javoy et al., 1986]. The range in $\delta^{13}C$ in these areas is a function of magmatic processes, source material involved in the melting, and fractionation of CO_2 upon degassing from melt [Javoy et al., 1978; Des Marais and Moore, 1984; Javoy et al., 1986]. The $\delta^{13}C$ values for high-temperature volcanic gases (considered to be representative of gases derived from magma) [Allard, 1983] in subduction zones average about $-4‰$ at Mt. Etna, Italy [Allard et al., 1997], $-3‰$ in the Sunda and Banda arcs, Indonesia [Poorter et al., 1991], $-2.9‰$ at Momotombo in Nicaragua [Allard, 1980], and $-2.7‰$ at Arenal in Costa Rica [Delorme et al., 1981]. Interpreting Figure 7 as a mixing line between modern biogenic CO_2 and magmatic CO_2 suggests that the magmatic source near Barva (with $^{14}C = 0$ pM) would have $\delta^{13}C = -2.6‰$, in excellent agreement with the direct measurements on nearby Arenal and Momotombo.

[29] The He data provide additional support for the hypothesis of a magmatic source for dissolved gases in bedrock groundwater. The R/R_A of bedrock groundwater is about 6.9 (Table 2). Similar high values of R/R_A have been found in other subduction zone settings influenced by magmatic gases: R/R_A 5.8–8.0 around the Pacific rim except for a few low values in Indonesia [Poreda and Craig, 1989], R/R_A up to 6.9 [Allard et al., 1997], R/R_A up to 6.7 [Fischer et al., 1998], R/R_A up to 4.5 [Evans et al., 2002], and R/R_A up to 5.6 [Sumino et al., 2004]. Magmatic gases are the only plausible explanation for values this far above the atmospheric value of 1.

[30] The $^{36}Cl/Cl$ of bedrock groundwater (17×10^{-15} at Guacimo Spring) is consistent with previously published values for Cl derived from magmatic outgassing and/or weathering of volcanic rocks. Hurwitz et al. [2005] concluded that magmatic outgassing was responsible for elevated [Cl] in groundwater of the Cascade Range (Oregon), and $^{36}Cl/Cl$ in groundwater from the area was $7–12.3 \times 10^{-15}$. Hedenquist et al. [1990] suggest a deep, possibly magmatic source of Cl may be responsible for the low $^{36}Cl/Cl$ of deep groundwater (about 3×10^{-15}) in the Mokai geothermal area of New Zealand. Rao et al. [1996] report that Cl in magmatic fluids condensed out of high-temperature fumaroles at four volcanoes was found to have $^{36}Cl/Cl < 15 \times 10^{-15}$. Phillips et al. [1995] did not report the $^{36}Cl/Cl$ of volcanic Cl but concluded that inputs of this Cl are likely the reason for the $^{36}Cl/Cl$ of Mono Lake in California being about 7.5X lower than that of local precipitation. Also, the mean $^{36}Cl/Cl$ values presented by Phillips [2000] for granitic rocks (25×10^{-15}) and basaltic rocks (7×10^{-15}) bracket the value at Guacimo Spring (17×10^{-15}), consistent with the overall intermediate composition of the andesitic-to-basaltic lavas of Volcan Barva [Alvarado-Induni, 1990]. Thus, geochemical/isotopic data and study site geology point strongly to magmatic outgassing and/or volcanic rock as the source for the C, He, and Cl acquired in the subsurface by bedrock groundwater in the rain forest near LSBS.
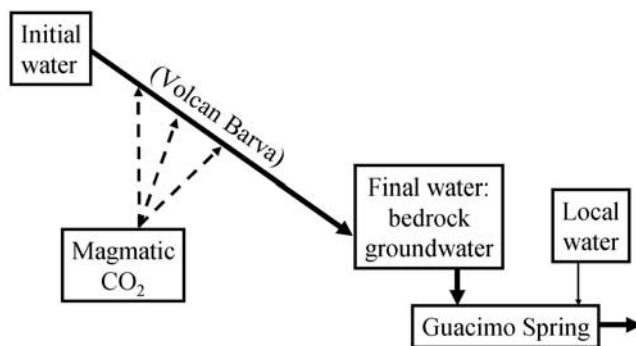
Figure 8. Conceptual diagram for NETPATH simulations to estimate the age of bedrock groundwater.

4.4. Age of Bedrock Groundwater

[31] We estimated the ^{14}C age of bedrock groundwater, using our geochemical and isotopic data in relatively simple simulations with NETPATH, a geochemical mass balance program [*Plummer et al.*, 1994]. In each NETPATH simulation, "initial water" (recharge to the bedrock groundwater system on the flanks of Volcan Barva) acquired magmatic CO_2 as it moved downgradient in the bedrock groundwater system (Figure 8). The water to be dated, bedrock groundwater, then mixed with a small amount of low-solute local water during discharge at Guacimo Spring (as suggested by very low but nonzero CFC concentrations in the spring water). Geochemical reactions in the simulations were simple (carbonate equilibria and oxidation of DOC), reflecting the simple situation of a volcanic rock aquifer without significant solid carbonate phases or solid organic matter, and subsurface acquisition of carbon from a single dominant source (magmatic CO_2). Thus, NETPATH was used only to automate the calculations of bedrock groundwater age, not to solve for all mass transfers (i.e., silicate weathering) between bedrock groundwater and the aquifer.

[32] We used two different approaches to modeling the "initial water" in our NETPATH simulations (Table 4),

each defined with combinations of field data and reasonable assumptions for unmeasured (and less important) variables. In approach 1, the DIC and DOC concentrations, and the $\delta^{13}C$ of DIC, were taken as averages of the measured values in local groundwater at wells 7, 14, 16, and 18. In approach 2, the DIC and DOC concentrations, and the $\delta^{13}C$ of DIC, were taken as the measured values at site BCNP1.

[33] Approach 1 has the advantage of being based on more than one sample, while approach 2 has the advantage of being based on a groundwater sample collected at higher elevation (about 660 m) in the suspected recharge area for bedrock groundwater [*Genereux*, 2004]. We used each approach in separate simulations.

[34] Nonnormalized ^{14}C values were used in all simulations, as is appropriate for age-dating calculations [*Plummer et al.*, 2004]; to this end, normalized values reported in Table 2 were "denormalized" (Table 4) using the equation given by *Mook and van der Plicht* [1999] and *Plummer et al.* [2004, p. 37]. We assumed that the ^{14}C of DIC in the initial water was 100 percent modern carbon (pmC), nonnormalized for isotope fractionation, a reasonable assumption for shallow "prebomb" groundwater in a recharge area in which biogenic soil CO_2 is expected to be the dominant source of DIC (the recharge area for bedrock groundwater is on volcanic rock, lacks limestone, and receives about 8 m of precipitation annually on the basis of unpublished 1990–2006 data collected at a nearby lodge located upslope from LSBS on Volcan Barva at an elevation about 600 m above LSBS; see www.rara-avis.com).

[35] Assumptions concerning the $\delta^{13}C$ and ^{14}C values of DOC were needed for the simulations but results are not very sensitive to these assumptions, mainly because [DOC] ≪ [DIC] (DOC accounted for 0.3% of TDC at Guacimo Spring, and about 8% and 2% of TDC in initial water under approaches 1 and 2 above, respectively; see Table 4). A $\delta^{13}C$ value of −25‰, a common assumption in ^{14}C groundwater dating studies [*Plummer et al.*, 1990; *Geyh*, 2000; *Plummer and Sprinkle*, 2001], was assumed for DOC in initial water and in all waters in the simulations (Table 4).

Table 4. Input Data on Carbon and CFC-12 for NETPATH Simulations

Parameter	Initial Water: Approach 1	Initial Water: Approach 2	Magmatic CO_2	Local Water	Guacimo Spring	Final Water[a]
DIC (mM)	1.42[b]	1.82[c]	NA[d]	1.42[b]	13.92[e]	14.53[f]
DOC (mM)	0.13[b]	0.04[c]	NA[d]	0.13[b]	0.04[e]	0.036[f]
TDC (mM)	1.55[g]	1.86[g]	NA[d]	1.55[g]	13.96[g]	14.566[g]
$\delta^{13}C$ DIC (‰)	−24.8[b]	−26.43[c]	−2.6[h]	−24.8[b]	−4.89[e]	−4.80[f]
$\delta^{13}C$ DOC (‰)	−25[i]	−25[i]	NA[d]	−25[i]	−25[i]	−25[i]
[14]C DIC (pmC)	100[i]	100[i]	0[i]	110.6[b,j]	8.26[e,j]	7.77[f,j]
[14]C DOC (pmC)	100[i]	100[i]	NA[d]	not needed	not needed	50, 100[k]
CFC-12 (pmol/kg)	0[i]	0[i]	NA[d]	1.672[b]	0.07815[e]	0[i]

[a]The final water in each simulation was bedrock groundwater; on the basis of CFC-12 concentrations, bedrock groundwater makes up 95.32% of Guacimo Spring water (the other 4.68% is young local groundwater mixing with bedrock groundwater at/near the spring outlet).

[b]Average for young local water in wells 7, 14, 16, and 18 (for DIC in wells 7 and 16, and DOC in well 16, the value used in calculating the four-well average was half the upper limit reported in Table 1).

[c]Measured value for high-elevation sample BCNP1.

[d]NA, not applicable (magmatic CO_2 is a gas phase; other columns represent waters).

[e]Measured value for Guacimo Spring. Measured [DOC] was below the limit of detection (0.08 mM); half this limit (0.04 mM) was the assumed concentration.

[f]Calculated from the mixing proportions stated above in footnote a and data in the table for local water and Guacimo Spring.

[g]TDC = DIC + DOC.

[h]The $\delta^{13}C$ of magmatic CO_2 from Figure 7.

[i]Assumed (see text).

[j]Nonnormalized for isotope fractionation [*Plummer et al.*, 2004, p. 37].

[k]Simulations were done with two different assumed values: 50 and 100 pmC (see text).

Table 5. NETPATH Results Concerning the Age of Bedrock Groundwater

Approach to Initial Water[a]	^{14}C of DOC in BGW (pmC)[a]	True δ^{13}C of DIC in BGW[a]	Simulated δ^{13}C of DIC in BGW[b]	Age of BGW[b] (years)	$\bar{v}$ of BGW[c] (m/a)
1	50	−4.80	−4.91	2500	3.6
1	100	−4.80	−4.91	2400	3.7
2	50	−4.80	−5.58	4000	2.3
2	100	−4.80	−5.58	3800	2.7

[a]See Table 4 and associated text in section 4.4.
[b]NETPATH result.
[c]Average linear velocity of bedrock groundwater (horizontal straight-line distance from the suspected recharge area on Volcan Barva to Guacimo Spring, divided by the groundwater age).

The assumption is within the range of measured values for DOC in nonvolcanic aquifers in Canada [*Wassenaar et al.*, 1990; *Aravena and Wassenaar*, 1993; *Aravena et al.*, 1995]; we are not aware of analogous data for tropical volcanic aquifers. The ^{14}C values in DOC span a wide range, e.g., from about 1 to 101 pM for groundwaters in Canada [*Wassenaar et al.*, 1990; *Aravena and Wassenaar*, 1993], depending on the age of the groundwater and sources of DOC (e.g., modern plant materials in the recharge area versus ancient sedimentary carbon). We assumed that DOC in initial water on Volcan Barva had ^{14}C = 100 pmC, reflecting DOC derived from relatively young (with respect to the ^{14}C half-life, 5730 years) soil organic matter in the absence of old sedimentary carbon. For simplicity dissolved O_2 was not included in the simulations but it must have been the electron acceptor for the small amount of DOC oxidation in the groundwater (the discharge at Guacimo Spring had significant dissolved O_2, 4.1 mg/L). Making the assumption that magmatic CO_2 outgassed beneath Barva is essentially free of ^{14}C because of a long residence time in a subduction zone magmatic system leads to an estimate of δ^{13}C = −2.6‰ for this CO_2 (Figure 7).

[36] The "final water" in the NETPATH simulations (the water to be dated) was bedrock groundwater. Data from Guacimo Spring give a good indication of bedrock groundwater chemistry, but the presence of low but nonzero CFC concentrations in the spring water suggests that a small amount of young (<50 years) local groundwater mixes with bedrock groundwater to form the spring outflow (Table 4). Thus, we carried out simple "unmixing" calculations on the basis of CFC-12 (CFC-113 gave essentially identical results), to estimate the chemical and isotopic characteristics of "pure" bedrock groundwater (i.e., Guacimo Spring water with the small amount of local water unmixed, mathematically). This calculated bedrock groundwater was then used as the "final water" in the NETPATH simulations. The local water unmixed from Guacimo Spring water in these calculations (fifth column in Table 4) was assumed to have the same chemistry as the initial water under approach 1, with two exceptions: (1) it was assumed to have modern, not "prebomb," ^{14}C content, and (2) its CFC-12 concentration was taken not as zero but as the average of those at wells 7, 14, 16, and 18 (Table 4).

[37] This approach to the mixing of local groundwater and bedrock groundwater at Guacimo Spring suggests the spring outflow is about 95% bedrock groundwater and 5% local groundwater. Using these mixing proportions (as calculated to two decimal places, 95.32% and 4.68%), we calculated the [DIC], [DOC], and the δ^{13}C and ^{14}C of DIC

for bedrock groundwater (last column in Table 4). For example, [DIC]$_{BGW}$ = (1/0.9532){13.92 mM − (0.0468)(1.42 mM)} = 14.53 mM.

[38] Finally, we assumed (and ran simulations with) two different values for ^{14}C in the DOC of bedrock groundwater (50 and 100 pmC, Table 4). The values were chosen to bracket the likely range of reasonable values, on the basis of the range of groundwater ages ultimately indicated by the simulations, if there was little or no isotopic exchange between DOC and DIC as the DOC moved through the bedrock groundwater system (this latter condition is possible for high molecular weight DOC, but may not be realistic for low molecular weight DOC [*Wassenaar et al.*, 1991]).

[39] Among the four NETPATH simulations (approaches 1 or 2 for initial water, and ^{14}C of 50 or 100 pmC in the DOC of final water), the age of bedrock groundwater falls in the range of about 2400–4000 years (Table 5). If agreement between measured and simulated δ^{13}C of DIC in the final water is taken as a measure of the quality of the simulation [e.g., *Plummer and Sprinkle*, 2001], then the better simulations are those in which approach 1 is used for the initial water. These two simulations place the bedrock groundwater age in the range 2400–2500 years (ages consistent with the DOC in bedrock groundwater having ^{14}C between 50 and 100 pmC if there is no isotopic exchange between DOC and DIC).

[40] It is generally recognized that diffusive loss of ^{14}C from active flow zones (from aquifer to aquitard, or, at a smaller scale, fracture to matrix), if it occurs and is not accounted for, may lead to overestimates of ^{14}C age for the groundwater in aquifers. Available data suggest the hydrogeology of the study site (Figure 9a) does not fit the situation of concern for large-scale diffusive loss from aquifers to aquitards [e.g., *Sanford*, 1997], mainly because of abundant downward leakage from one lava aquifer to another through the ignimbrite layers that function as "leaky" aquitards [*Parker et al.*, 1988; *Foster et al.*, 1985]. However, it is not possible to rule out the overestimation of age by fracture-matrix exchange of ^{14}C [*Neretnieks*, 1981]; even without geochemical effects age may be overestimated by an amount that increases with the ratio of total porosity to fracture porosity [*Maloszewski and Zuber*, 1991]. Fracture porosity is not known for the ignimbrite, tuff, and lava sequences of Barva (and there are few field-scale estimates for any rock masses), but effective matrix porosity is roughly 0.15 for lavas and ignimbrites; effective matrix porosity is about 0.55 for tuffs, but these strata are more permeable and groundwater flow is not limited to fractures [*Foster et al.*, 1985]. Assuming lava
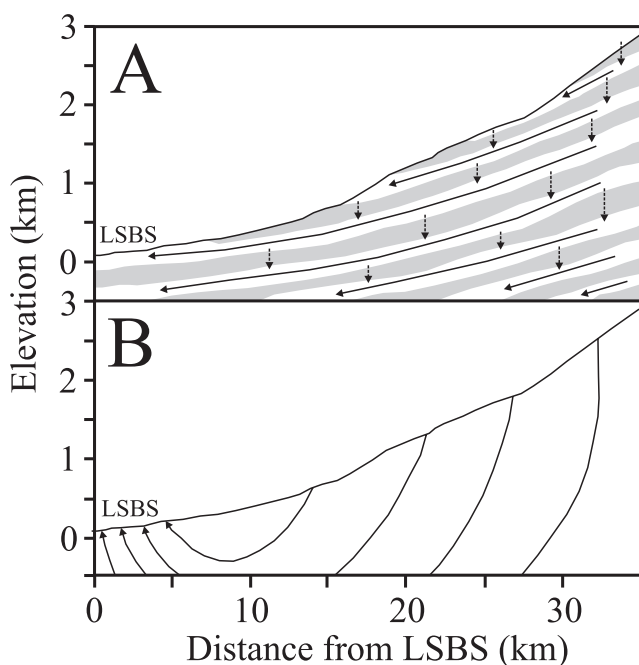
Figure 9. (a, b) Alternate conceptual models for groundwater flow paths on Volcan Barva. The model in Figure 9a, lateral downslope flow in lavas (white) and vertical leakage between lavas in ignimbrites (gray), is more likely based on the physical hydrogeological work on the south side of Barva and the tracer work on the north side, at and near La Selva Biological Station. Vertical exaggeration is 5X.

and ignimbrite fracture porosities of 0.05 to 0.45 (one third to three times matrix porosity), and assuming groundwater flow occurs in the fractures but not matrix, diffusion effects could be responsible for overestimation of age by factors of about 4 to 1.3 (total porosity divided by fracture porosity).

[41] Estimates of average linear velocity in the bedrock groundwater (2.3–3.7 m/a, Table 5) were calculated by dividing the bedrock groundwater ages into the straight-line horizontal distance (9 km) between Guacimo Spring and the recharge area suggested by *Genereux* [2004]. At present there is no independent way to quantitatively evaluate these values of average linear velocity. These values of average linear velocity might be best viewed as lower limits (they would be higher if the diffusion effects mentioned above occur in the bedrock).

4.5. Carbon Inputs to Lowland Watersheds via IGF

[42] Previous work at LSBS shows large inputs of water and major ions to lowland rain forest watersheds by IGF [*Genereux et al.*, 2002, 2005]. Those results, together with the [DIC] and C isotope data presented here for bedrock groundwater, suggest that IGF is also responsible for a large input of (mainly magmatic) carbon to this lowland rain forest. For example, annual water budget results for the Arboleda watershed over 4 consecutive 12-month budget periods (December 1998 to November 2002) showed that the 50 ha watershed received on average 4370 mm/a of bedrock groundwater and 5590 mm/a of local groundwater by IGF [*Genereux et al.*, 2005]. IGF of local groundwater

may reflect subsurface mixing of local and regional (bedrock) groundwaters across the interface between the two systems [*Genereux et al.*, 2005]. We multiplied these groundwater input rates by the [DIC] and [DOC] of bedrock groundwater and local water (Table 4), respectively, to estimate the annual carbon input to the Arboleda watershed by IGF.

[43] The total calculated input of carbon to the Arboleda watershed by IGF is about 2.29 μmol of C per m^2 of watershed area per second (μmol/m^2 s). DIC accounts for 98.7% of this, DOC about 1.3%. Also, about 88% of C input is due to bedrock groundwater (in which about 89% of TDC is from magmatic CO_2), only 12% to local water. The IGF-based input of carbon to the Arboleda watershed is nontrivial with respect to other large ecosystem-level carbon fluxes. For example, it is 24–32% of whole ecosystem respiration, estimated as 7.05 μmol/m^2 s [*Loescher et al.*, 2003] to 9.40 μmol/m^2 s [*Cavaleri et al.*, 2008]. It also falls near the upper end of the range for net ecosystem exchange (NEE) of CO_2 with the atmosphere: about 0 to 2.1 μmol/m^2 s, depending on the year and the method used [*Loescher et al.*, 2003] (NEE is not a single flux but rather the net sum of input and output fluxes between the ecosystem and atmosphere).

[44] The fate of the carbon from IGF is to be discharged to surface water (wetlands and streams) along with the groundwater in which it is dissolved, from where the DIC may volatilize to the atmosphere and both DOC and DIC may be exported from the watershed via streamflow (some DOC may also decompose to DIC). Some of the CO_2 that volatilizes from surface water may subsequently be taken up by vegetation within the surrounding forest. We are currently looking for isotopic evidence of magmatic carbon in plants at LSBS, as has been found in other volcanic landscapes [*Pasquier-Cardin et al.*, 1999; *Cook et al.*, 2001]. Work is also currently underway to quantify watershed export of DIC and DOC at the weirs on the Arboleda and Taconazo watersheds, using data on stream discharge and stream water [DIC] and [DOC]. As suggested by *Cole et al.* [2007], knowledge of this export may be important to understanding the carbon budgets of watersheds and not overestimating the extent to which watersheds function as CO_2 sinks. As another hydrologic pathway for transport of C, IGF may also play a role in the overall carbon budgets of watersheds and their ecosystems.

5. Conclusions

[45] There are wide ranges of concentrations and isotopic ratios of C, He, and Cl in groundwater and surface water of the lowland rain forest in and near La Selva Biological Station (LSBS), Costa Rica. The data are strongly consistent with the presence and mixing of two hydrogeochemically distinct groundwaters: (1) bedrock groundwater, a relatively high-solute groundwater that represents interbasin groundwater flow (IGF) into the lowland rain forest watersheds, and (2) local groundwater, a more dilute groundwater that is recharged locally in the lowlands.

[46] The data offer strong evidence that the elevated C, He, and Cl concentrations in bedrock groundwater are derived from outgassing of a magmatic source or weathering of andesitic-basaltic rock formed from this magma, most likely beneath nearby Volcan Barva. This result seems

consistent with the conclusions of *Pringle et al.* [1993] concerning volcanic sources for other solutes at LSBS. High $\delta^{13}C$ (−4.89‰), low ^{14}C (7.98 pM), high R/R_A for He (6.88), and low $^{36}Cl/Cl$ (17 × 10^{-15}) at Guacimo Spring are all strong indications of this. Also, extrapolation to zero ^{14}C of a highly linear $\delta^{13}C - {}^{14}C$ relationship ($r^2 = 0.984$) suggests the carbon source to bedrock groundwater has $\delta^{13}C = -2.6$ ‰, almost identical to the measured $\delta^{13}C$ of CO_2 in high-temperature gases from two volcanoes in the region (−2.7‰ at Arenal, −2.9‰ at Momotombo).

[47] Results support the hypothesis of a large age difference between bedrock groundwater and local groundwater. Dating of ^{14}C places the age of bedrock groundwater in the range 2400–4000 years (with a best estimate probably at the lower end of that range). Local groundwater has ^{14}C concentrations in excess of 100 pM, indicating the presence of anthropogenic "bomb carbon" and thus ages less than about 55 years for these samples collected in 2006. More specific age estimates for local groundwater, based on CFC and SF_6 data, are presented in a companion paper (Solomon et al., submitted manuscript, 2009).

[48] C, He, and Cl concentrations and isotope ratios are fully consistent with the conceptual hydrologic model previously presented for this region: most of the large variation in solute concentrations can be explained by the presence and mixing of two distinct groundwaters (the two mentioned above), bedrock groundwater is much older than local groundwater, the elevated solute load of bedrock groundwater is related to its subsurface residence time in volcanic rock, and local groundwater has not had significant interaction with volcanic rock.

[49] Considering the present work together with previous publications [*Pringle et al.*, 1990, 1993; *Genereux and Pringle*, 1997; *Genereux et al.*, 2002, 2005; *Genereux*, 2004; *Genereux and Jordan*, 2006], it is promising to find a highly consistent hydrologic interpretation for such a wide range of observations: aqueous concentration data (C, He, Cl and other major ions, P, Si), isotopic data (for C, He, Cl, O), and physical hydrologic data (precipitation, stream discharge, and evapotranspiration values used to develop water budgets). Solomon et al. (submitted manuscript, 2009) extends this list to include noble gases beyond He and anthropogenic trace gases with age-dating capabilities for young groundwater (SF_6, CFCs). This provides confidence in the hydrologic interpretation, and in the fidelity of different approaches (physical, chemical, and isotopic, including tracers with different geochemical behaviors) as they converge on the same solution for the same system.

[50] Past work on the hydrogeology of the south flank of Volcan Barva has stressed the layered anisotropic character of the rocks, significant downslope flow of groundwater in lavas, and slower vertical flow through less permeable ignimbrites between lavas [*Foster et al.*, 1985; *Parker et al.*, 1988] (Figure 9a), rather than flow lines arcing deeply downward and then upward through the full rock mass of Barva (Figure 9b). The latter model (Figure 9b) implies that bedrock groundwater might discharge with a broad range of ages and chemical compositions in the lowlands, a result that seems unlikely on the basis of the tracer data reported here and previously. Figure 9b would also suggest an elevated temperature for some bedrock groundwater, a result not consistent with our data. The model in Figure 9a is more consistent with both the hydrogeologic work of others and our tracer data.

[51] Unlike many well-studied sites in North America and elsewhere, there is as yet no direct access to the regional bedrock groundwater system through deep wells. All water sampling has been in surface seeps, streams, and shallow (≤2 m) wells in the lowland rain forest where local groundwater and bedrock groundwater mix (and one small seep farther upslope on Barva, BCNP1). Even without a network of deep wells the LSBS-BCNP corridor (Figure 1) makes an excellent field laboratory for measurements, experiments, and hypothesis testing related to IGF and linked tectonic-volcanic-hydrological-ecological processes. Transport of magmatic CO_2 into the lowland rain forest by IGF appears to be significant relative to other large ecosystem-level CO_2 fluxes, and other hydrologic fluxes of C (e.g., export from watersheds via streamflow) may also be significant. The importance of these fluxes to the biota and watershed-level C budgets, and their potential response to climate change, are not currently known and merit study.

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