# GROUNDWATER-SURFACE WATER INTERACTION AND NITRATE ORIGIN IN VOLCANIC AQUIFERS, CENTRAL VALLEY, COSTA RICA

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**Abstract.** Deterioration of groundwater quality by anthropogenic input of nitrate is a significant issue in Costa Rica's Central Valley. Nearly 60% of the Central Valley's municipal water supply is derived from volcanic aquifers. Groundwater nitrate concentrations have been steadily increasing in recent years, reaching levels above or near the WHO drinking water standard. Groundwater–surface water interactions in the system are complex. Rivers are alternately effluent and influent depending on the geology and season (wet or dry) and could thus either receive or contribute to groundwater nitrate. An attempt to estimate groundwater recharge elevations using isotopic composition of precipitation and springs was hampered by an apparent reverse altitude effect. The correlation between nitrate and chloride concentrations in a water supply spring and a well suggests the nitrate is derived from domestic sewage. This contrasts with a domestic well with nitrate apparently derived from commercial fertilizer applied to coffee plantations. Consistently low river nitrate concentrations suggest most of the groundwater nitrate reaches the aquifers by direct infiltration on the land surface and not through leakage below influent river sections.

**Keywords:** volcanic aquifers, nitrate, Costa Rica, groundwater -surface water interactions, precipitation isotopes

## INTRODUCTION

The Central Valley is a topographical depression in Costa Rica's central highlands surrounded by active and inactive volcanoes (Figure 1). The valley is dominated by the City of San Jose and many smaller municipalities, and contains almost half the country's 3 million people. Groundwater provides about 60% of San Jose's drinking water and also supplies most of the smaller municipalities. The groundwater in Central Valley is naturally vulnerable to contamination from surficial sources due to the high annual precipitation (2000 to 5000 mm) and the relatively high permeability of the unsaturated zone (Reynolds-Vargas et al. 1995). In the last decade, nitrate concentrations in the municipal water supply aquifers have been steadily rising (BGS/SENARA 1988; Rodriguez-Estrada and Loaiciga 1995). The suspected sources are the commercial fertilizers applied on coffee plantations (average rate 270 kg N/ha/year in 2001; Reynolds-Vargas and Richter 1995), and domestic sewage disposed into rivers or beneath the land surface in latrines. The relative contribution of these sources is unclear as is the predominant pathway(s) by which the nitrate enters the groundwater system. The groundwater - surface water interaction is complex, with rivers alternately influent (losing to groundwater) or effluent (gaining from groundwater) along their reaches. The purpose of this study is to investigate nitrate origin(s) and groundwater – surface water interactions in a small watershed that is hydrogeologically representative of the region.

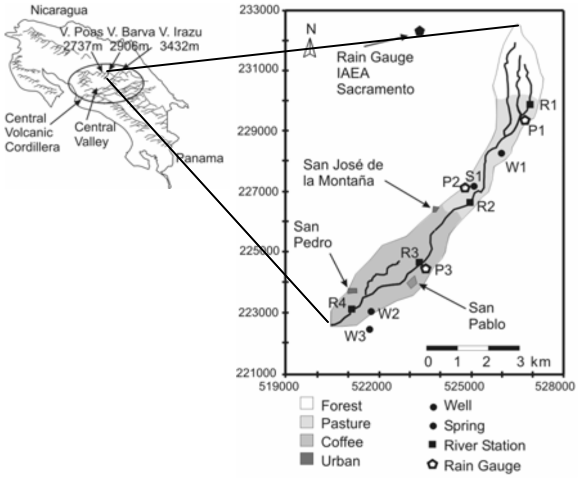

**Figure 1** Location of and land use within the Macarrón watershed groundwater - surface water interaction

### Study Area

The 12.5 km$^2$ Upper Mancarrón River watershed is located in the north-eastern section of the Central Valley (Figure 1), and consists of natural forests, coffee plantations, and urban areas (Figures 1 and 2). The 12.7 km long river reach is located between the 1,100 and 2,340 masl, has an average slope of 11% and a single tributary. The two major aquifer formations are the Barba and Colima Formations, separated by the thin and leaky Tiribi aquitard. The Barba Formation, up to 95 m thick, is comprised by the Los Angeles and Los Bambinos (LA/LB) aquifers, including independent shallow andesitic-basaltic lava flows forming discontinuous perched aquifers separated by the Porrosatí and Carbonal aquitards. The LA/LB aquifers are exposed in the upper section of the watershed and generally discharge in springs at lower elevations. The second aquifer in the Barba Formation is the Lower Barba aquifer (LBa) comprised of highly vesicular basaltic-andesitic lava with high porosity and high fracture and breccia permeability. Groundwater from the LBa discharges into springs or rivers, or leaks into the Colima Formation. The upper and lower Colima aquifers from the Colima Formation are extensively exploited for water supply (Darling et al. 1989).

## MATERIALS AND METHODS

The watershed was divided in four reaches by four river sampling stations and a spring (R1, R2, R3, R4 and S1; Figure 2). River discharge was estimated using a graduated cylinder and stopwatch. Water samples were collected from June 22, 2000 to April 18, 2001 at these sampling locations, as well as three domestic wells (W1 to W3), and three rain gauges (P1 to P3; Figures 1 and 2). Monthly composite samples of precipitation were collected for $^{18}O$ and D for all months except May and June. Isotopic ratios for these months were interpolated from the IAEA Sacramento station and P1 isotopic composition for April and July (Marchand 2001).

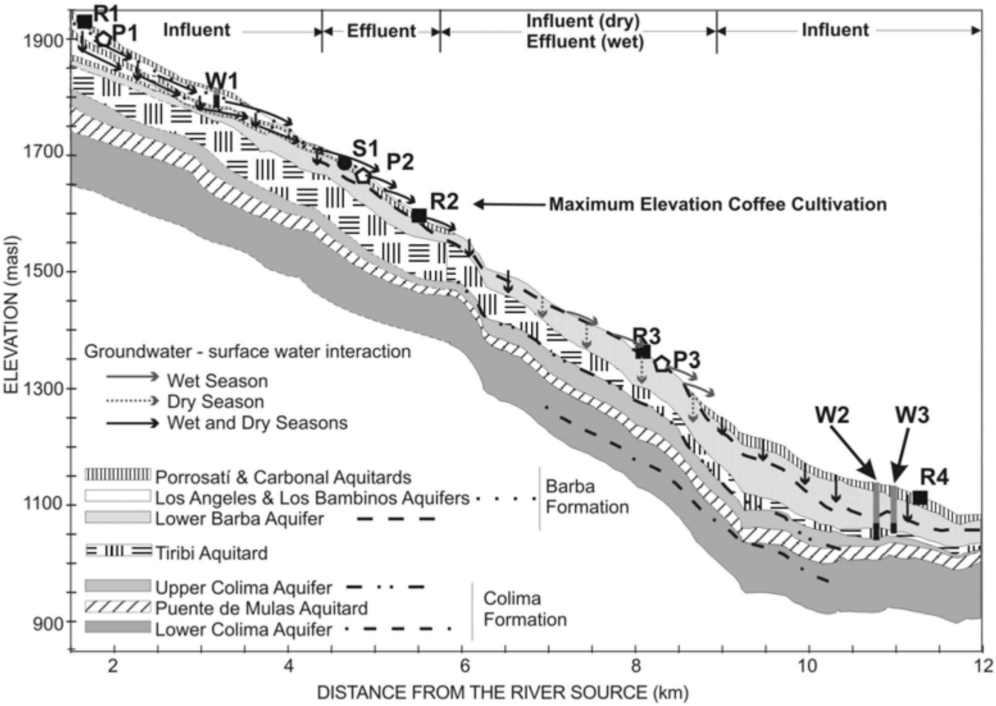

**Figure 2** Geologic cross section along the Mancarrón River valley. Nature of groundwater – surface water interaction indicated by labels at top of figure and arrow on diagram. Water levels in individual aquifers indicated on figure and legend. (Groundwater levels interpolated from BGS/SENARA, 1988 and field data).

Nitrate and chloride were analysed on a Technicon Autoanalyzer (Industrial Method Nos. 100-70W/B and 99-70W, respectively). Deuterium analyses were conducted by reduction of water hydrogen with zinc at 500ºC (Coleman 1982) using a VG 602 double collector mass spectrometer. $^{18}O$ analyses were carried out by the standard Epstein-Mayeda (1953) carbon dioxide equilibration method using a VG 903 triple collector mass spectrometer. Results are reported in standard $\delta$ notation relative to V-SMOW.

## RESULTS AND DISCUSSION

Groundwater – surface water interaction, as indicated by seasonal stream discharge in the Mancarrón River, is complex. While the highest and lowest elevation river reaches are consistently influent (i.e. river water always recharges groundwater; Figure 2), intervening sections are either effluent, or alternate between influent and effluent depending on seasonal groundwater levels.

Isotopically the river and groundwaters are consistent with the local meteoric water line (LMWL) obtained from the three rain gauges ($\delta^2H = 8.5\ \delta^{18}O + 14.9$; $r^2 = 0.99$; Marchand, 2001) and similar to LMWLs observed in other studies in the Central Valley (BGS/SENARA 1988; Darling et al. 1989). The usual “altitude effect”, causing more depleted waters with increasing altitude, is observed at the lower elevation sampling stations (Clark and Fritz 1997, Table 1). However, a “reverse altitude” effect occurred at higher elevations, where waters were observed to have a more enriched $^{18}$O and D ratio with increasing altitude (Table 1). This is attributed to the transport of relatively enriched precipitation from the Atlantic Ocean (Lachinet and Patterson 2002), to the Pacific side of the volcano, particularly between October and February. Precipitation derived from the Pacific Ocean, depleted relative to that from the Atlantic Ocean, tends to occur from March to September (BGS-SENARA 1988; Darling 1989). Higher elevation groundwaters (W1 and S1 - LA/LB aquifers) also tended to be isotopically enriched relative to lower elevation groundwater (W2 and W3 – LBa aquifer; Table 1). A comparison of groundwater and rainwater isotopic composition suggests that the LBa aquifer (W2 and W3) is recharged at moderate elevation (1,650 masl or less).

**Table 1** Average, standard deviation (in brackets following average), and number of analyses (n) for isotopic and geochemical analyses of rain (P, estimated annual volume-weighted average), groundwater (S and W), and river (R) water samples. The well depths and screened aquifer are noted.

| **Name** | **Type** | **Elevation** (masl) | **$\delta^{18}$O (‰)** | **$\delta^{2}$H (‰)** | **NO$_3^-$ (mg N/L)** | **Cl$^-$ (mg/L)** | **n** |
|---|---|---|---|---|---|---|---|
| **P1** | Rain | 1,900 | -8.0 (0.2) | -53.1 (1.7) | ---- | ---- | 12 |
| **P2** | Rain | 1,650 | -8.8 (0.3) | -59.5 (2.1) | ---- | ---- | 12 |
| **P3** | Rain | 1,340 | -8.6 (0.3) | -57.4 (2.0) | ---- | ---- | 12 |
| **W1** (43 m/LA/LB) | Well | 1,820 | -8.4 (0.4) | -55.1 (2.8) | 0.1 (0.1) | 1.0 (0.1) | 37 |
| **S1** ( --- / LA/LB) | Spring | 1,600 | -8.7 (0.2) | -56.0 (1.3) | 0.9 (0.5) | 1.9 (0.3) | 40 |
| **W2** (110 m/ LBa) | Well | 1,140 | -9.1 (0.2) | -62.4 (1.5) | 3.4 (1.4) | 2.9 (0.3) | 37 |
| **W3** (93 m/ LBa) | Well | 1,130 | -9.2 (0.3) | -62.2 (1.4) | 2.8 (1.2) | 3.1 (0.3) | 32 |
| **R1** | River | 1,920 | -6.8 (0.5) | -40.2 (2.7) | 0.1 (0.1) | 0.6 (0.1) | 40 |
| **R2** | River | 1,625 | -8.2 (0.7) | -51.2 (4.9) | 0.1 (0.1) | 1.3 (0.3) | 40 |
| **R3** | River | 1,340 | -8.4 (0.9) | -55.1 (5.6) | 0.3 (0.4) | 2.2 (0.6) | 40 |
| **R4** | River | 1,120 | -8.4 (0.9) | -54.4 (6.3) | 0.3 (0.4) | 3.3 (1.8) | 30 |

## Nitrate and Chloride

Despite the observed input of raw sewage in surface water, nitrate was consistently low in the river (0.07-0.32 mg/L; Figure 4), suggesting rapid assimilation by river biota. Chloride in the rivers and groundwater is thought to be mainly derived from sewage (including animal manure). Low concentrations of nitrate and chloride in the highest elevation well (W1) suggest there is no water quality impact by either fertilizer or sewage. This is consistent with the lack of urbanization or agricultural activities at this elevation or higher in the watershed (Figure 1).

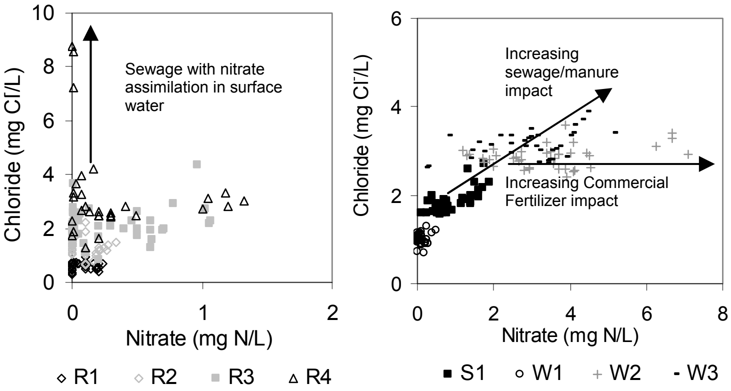

**Figure 4** Chloride versus nitrate in river waters and groundwaters.

If nitrate loss does not occur in groundwaters, a linearly increase in chloride and nitrogen concentrations is expected to be related to animal or human waste/sewage (Crites et al. 1998; DeSimone and Howes 1998). Increasing chloride concentrations in S1 and W3 are accompanied by corresponding increases in nitrate concentrations, suggesting their water quality is affected by sewage. The highest nitrate concentrations in these groundwaters (~4.5 mg N/L) are still well below the drinking water guideline of 10 mg N/L for nitrate. The moderate elevation well, W2, has variable nitrate concentrations (as high as ~7.5 mg N/L). The isotopic composition of the groundwater at W2 is consistent with groundwater recharged at moderate elevation (1,650 masl and lower) where coffee cultivation is extensive (Figure 1). The lack of a linearly increasing chloride and nitrate concentrations, and the estimated recharge elevation of W2 suggests that the elevated nitrate in this well is derived from fertilizer applied to coffee plantations.

## CONCLUSIONS

Groundwater-surface water interaction in the Mancarrón watershed is complex. While some reaches are consistently effluent or influent, others alternate depending on seasonal groundwater levels. The highest elevation groundwaters have no anthropogenic water quality impacts. Elevated nitrate and chloride in some groundwaters at lower elevation in the watershed suggest water quality is impacted by sewage. In other lower elevation groundwaters, elevated nitrate without corresponding increases in chloride suggest the nitrate is derived from commercial fertilizer from coffee plantations. The assimilation of nitrate in the river mitigates the nitrate issue in surface waters and suggests the river is not a significant source of groundwater nitrate.

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