Report

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Trends in Nitrate Concentrations and Determination of its Origin Using Stable Isotopes (^{18}O and ^{15}N) in Groundwater of the Western Central Valley, Costa Rica

A study was conducted to evaluate long-term trends in nitrate concentrations and to try to identify the origin of nitrate using stable isotopes ($^{15}N_{NO3}{}^{-}$ and $^{18}O_{NO3}{}^{-}$) in the aquifers of the western Central Valley, Costa Rica, where more than 1 million people depend on groundwater to satisfy their daily needs. Data from 20 sites periodically sampled for 4 to 17 years indicate an increasing trend in nitrate concentrations at five sites, which in a period ranging from 10 to 40 years, will exceed recommended maximum concentrations. Results of isotopic analysis indicate a correspondence between land use patterns and the isotopic signature of nitrate in groundwater and suggest that urbanization processes without adequate waste disposal systems, followed by coffee fertilization practices, are threatening water quality in the region. We conclude that groundwater management in this area is not sustainable, and that land use substitution processes from agricultural activity to residential occupation that do not have proper sewage disposal systems may cause a significant increment in the nitrate contaminant load.

INTRODUCTION

Groundwater is of great importance for many countries in the world, where most drinking water comes from aquifers (1). Aquifers have provided inexpensive drinking water for populations, a fact that can be associated with improvements in public health parameters and with many other socioeconomic benefits. Nevertheless, at the present time, the most important challenge is to attain sustainable management of groundwater in places where the quality of the resource is threatened. Groundwater quality degradation is related primarily to land use changes that do not take into account the effect on underlying aquifers.

Nitrate is the most common contaminant in groundwater, and is primarily derived from leaching of synthetic fertilizer and from on-site sewage disposal methods, especially in areas with medium or high population density (2). In developing countries, as in rural areas of industrialized nations, houses are not normally served by centralized sewerage systems; rather, they rely on on-site sanitation systems such as latrines and septic tanks. The public health standard limit on nitrate is 10 mg L^{-1} NO_3^{-}-N or 45 mg L^{-1} NO_3^{-}. Consumption of water containing high concentrations of nitrate can cause methemoglobinemia or the "blue baby syndrome" (2).

Nitrate is very soluble in water and is readily leached from soils dominated by permanent negative charges or soils with moderate to high pH, without being influenced by adsorption reactions. Previous research has provided evidence for the anion adsorption capacity of volcanic soils, which typically contain large amounts of amorphous materials such as allophane, aluminum and iron oxides, and hydroxides. Anion adsorption in this type of soils has been recognized as a potential mechanism for retarding nitrate leaching (3, 4). Nevertheless, the ability of Andisols to retard nitrate leaching by electrostatic adsorption is a function of a complex of interrelated soil properties, and as such, is highly variable (5). In addition, electrostatic forces that adsorb nitrate are typically weak, and their effectiveness as a protection of groundwater quality may be limited.

The Virilla River basin, located in the Central Valley of Costa Rica, is the most developed and most densely populated area in Costa Rica. In 1986, urban population covered approximately 11 percent of the area of the Virilla River basin, and increased to almost 30 percent in 2003 (Reynolds-Vargas, unpubl. data). Modifications in land use patterns for the last 30 y have been responsible for an increase in the amount of sediments in rivers and in the concentration of chemical and biological contaminants in surface and groundwater in the region. Most of the surface water, especially in urban areas, is polluted with agrochemical and industrial residues, and organic substances derived from inadequate waste disposal. Due to the low quality of river water and to the high cost of treatment to make it suitable for drinking, groundwater has been increasingly used since the 1960s. At present, more than 60 percent of the population in the main cities in the Central Valley obtains water from the volcanic aquifers that underlie the region. This percentage may increase to about 90 percent during the next 10 to 15 y to satisfy growing population demands (6).

Groundwater in this region generally has excellent natural chemical and bacteriological quality, and the costs associated with its use have been relatively low, because it can be distributed almost without any previous treatment. Nevertheless, aquifers are vulnerable to contamination because of the ease with which chemical substances derived from human activities can be transported through permeable soil and rock materials and because of the direct communication between shallow aquifers and polluted rivers. The contaminant travel time through the unsaturated zone may vary from several months to many years (7). For this reason pollution may not be detected immediately and may become an irreversible process in the short term or medium term. In addition, because pollution of the aquifers can have important economic and social implications, it is probable that the cost of protecting groundwater from contamination would be much lower than the cost of water or aquifer treatment. To recommend management practices and establish regulations, an urgent need exists to identify which chemicals potentially hazardous to human health are present in groundwater, to investigate the patterns of variation in contaminant concentration, and to learn about their origin and transport mechanisms through the unsaturated zone.

Groundwater contamination with nitrate already has been recognized as a potential problem in this region (8, 9) not only because high concentrations of nitrate in drinking water may cause health problems, but also because its presence may be an

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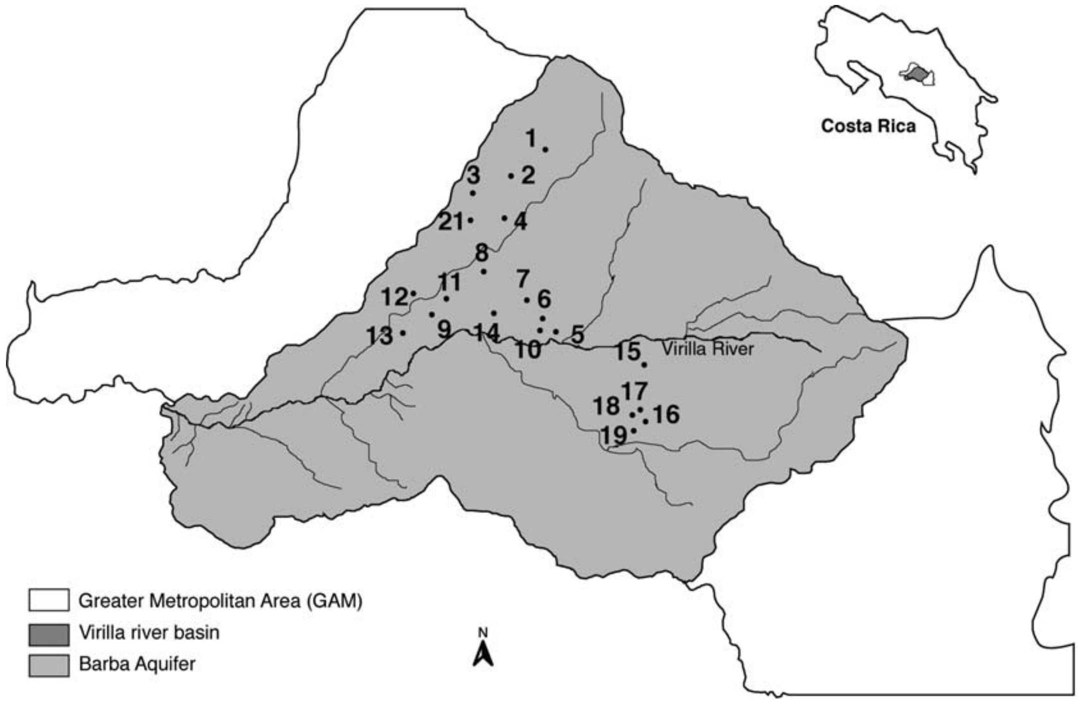

	Site Name
1	Pérez Spring
2	Birrí Spring
3	Guachipelín Spring
4	CICAFE Well
5	La Libertad Spring
6	W5 Well
7	La Esperanza Well
8	San Joaquín Well
9	Puente de Mulas Spring
10	W2 Well
11	Belén Spring
12	Ojo de Agua Spring
13	Potrerillos Spring
14	Barreal Well
15	Miravalles-Guaitil Well
16	Café Rey Well
17	PRENAC 1 Well
18	PRENAC 2 Well
19	Motel Camino Real Well
21	León Cortés Spring

Figure 1. Location of the Virillia River basin and sampling sites.

indirect indicator of the presence of other contaminants derived from human activities. Reynolds-Vargas and Richter (9) demonstrated that concentrations of nitrate vary along an elevation gradient in the Virilla River basin. On several occasions during a 2-y monitoring period, concentrations exceeded the maximum of 10 mg L^{-1} of NO_3^--N recommended by the World Health Organization. A correlation between high concentrations of nitrate and the seasonal rain pattern was observed: nitrate concentrations in groundwater appeared to be higher during the rainy season, especially in mid- and high-elevation springs and wells, but no particular trend in nitrate concentrations could be observed over time. As potential sources of nitrate contamination, Reynolds-Vargas and Richter mentioned on-site sanitation systems, nitrogen fertilizers applied to coffee plantations, and influent rivers that collect runoff from agricultural fields and sewage pipelines, and pointed out that although retardation of nitrate transport due to adsorption processes may be an important process in volcanic soils, adsorption might not be a reliable mechanism to hinder groundwater contamination.

Estimations of the total nitrate derived potentially from both fertilizer applications in agriculture and urban residential occupation have been made using semiquantitative analytical solutions using an estimation of the rates of nitrogen leaching, of water infiltrated from precipitation and from other sources, and an attenuation factor (10). Despite the limitations involved, it is possible to develop an estimate of the potential contaminant load into aquifers, at least in a relative manner. In agricultural areas it is important to note that leached nitrate is derived from the soil nitrogen pool as a whole, and only a small proportion will originate directly from fertilizer applied in any given year. The amount of organic fertilizer (manure and compost) applied to coffee plantations is not considered significant. Having studied the nitrogen balance on a coffee plantation in the Central Valley, Sommer (11) concluded that only 30 percent of the nitrogen added as fertilizer is effectively absorbed by the coffee plant. The rest is lost to the system, and most of it probably leaches below the root zone. Salas et al. (12) estimated that more than 50 percent of all nitrate applied was leached below the root zone and was not used by the plant. Their 2-y study on chemical fertilizer efficiency in coffee showed that on the average, only 45 percent of the nitrogen applied as fertilizer was used effectively by the coffee plant.

However, by far the most serious unknown is the rate of leaching loss of nitrates, which is a complex function of the interaction between the climate-precipitation regime and land use. According to Foster and Hirata (10), these problems can be overcome if it is assumed that agricultural production involves continuous, albeit partial, soil cover (such as coffee plantations) and that the production operates for a long period of time. According to the literature, these authors expect values between 20 and 50 percent as the percentage of nitrogen loss from fertilizer applications, although values such as 75 percent are sometimes found.

For nitrate originating from on-site sanitation systems, the greatest uncertainty is associated with the proportion of the deposited nitrogen that will be oxidized and leached in the groundwater recharge. A range of 20 to 60 percent is considered possible (13–15), but the actual proportion will depend on per capita water use, the proportion of losses of volatile nitrogen compounds, and the amount of nitrogen removed during cleaning of septic system facilities, which will vary depending on the type of installations involved. Considerable uncertainty may also surround the estimation of natural infiltration rates from excess rainfall.

This article includes results that are part of a comprehensive, long-term study conducted to evaluate the impact of agricultural and urban activities on groundwater in the Central Valley of Costa Rica. The specific objectives of this study were to *i)* determine trends in nitrate concentrations in groundwater, and *ii)* evaluate the potential usefulness of stable isotope analyses (^{18}O and ^{15}N) in nitrate from groundwater to identify the origin of contamination.

Use of Stable Isotopes

Because nitrate contamination in groundwater currently represents a widespread problem in many areas of the world (16), several researchers have attempted to use natural variations of $^{15}N/^{14}N$ ratios in nitrogen compounds, primarily nitrate, as

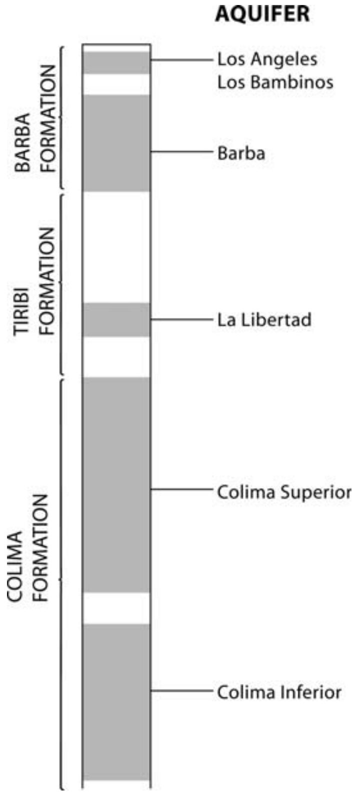

Figure 2. Simplified geological column of the Virillia River basin, modified from BGS/SENARA (8). See lithologic information in the text.

indicative of their origin (17–21). The decision to use $\delta^{15}N$ analysis is based on the fact that different sources of nitrate have distinct isotopic signatures. According to the literature (22, 23), isotopic composition varies from −12‰ to 3‰ in rainwater nitrate and from 3 to 8‰ in nitrate formed during organic matter nitrification. Nitrogen fertilizers usually have relatively low $\delta^{15}N$ values ranging from −5 to 7‰. In nitrate from human and animal excreta, concentrations of $\delta^{15}N$ vary from 8 to 22‰ (18).

Applications of $\delta^{18}O$ analyses for determining nitrate sources in groundwater are scarce, probably because of the complicated analytical methods involved (24). One study (25) acknowledged a limitation in the use of $\delta^{18}O$ as a tracer of the sources of nitrate in groundwater; due to the small differences observed in $\delta^{18}O$ values in nitrate derived from fertilizers and from human excreta.

There are some difficulties related to the interpretation of isotopic data. Once fertilizer N enters the soil it becomes involved in biological transformations in the soil-plant system, and in many cases loses its isotopic identity (26). Because isotopic fractionation is a common phenomenon in biological environments, some authors consider that only semiquantitative results can be expected. In spite of this, Letolle and Olive (27), among others, advocate that it is possible to determine the origin of nitrate contamination using the $^{15}N/^{14}N$ relationship in cases in which the number of nitrate sources is limited. The analysis of natural abundance of $^{15}N_{NO3}{}^{-}$ has proved successful on several occasions (25, 28), especially when nuclear techniques are combined with the use of other tracers and with results derived from conventional chemical analyses.

Study Area

The study was conducted in the western part of the Central Valley of Costa Rica, where more than 2 million people live (Fig. 1), half of whom depend on the aquifers to satisfy their water needs. This valley represents approximately 3 percent of the total area of the country and is surrounded by volcanic peaks reaching 3000 m asl (above sea level). The region is occupied primarily by the Great Metropolitan Area (in Spanish: *Gran Area Metropolitana* or *GAM*), and is actually a topographic depression at elevations ranging from 600 to 1500 m. Land use patterns have changed drastically in less than 2 decades in this region: between 1986 and 2003, the urban population increased by 54 percent (29, 30). Volcanic materials, derived mainly from the Barba Volcano during the Quaternary period, have formed a complex and highly vulnerable aquifer system, which is the main source of drinking water for the population.

Photo 1. Typical landscape at the high elevation areas in the Central Valley, Costa Rica. Photo: F. Barrantes.

The Virilla River basin has an area of 918 km^2. Its geological structure (Fig. 2) has been formed by pyroclasts of variable depth and porosity but with high infiltration capacity and lavas that are generally fractured and brecciated, with high hydraulic conductivity (31–33). Regional groundwater flow is from northeast to southwest, under high hydraulic gradients (8) that are often related to the relief at the base of the aquifer and may be similar to the gradient of the land surface. The Barba Formation comprises several lavas that have formed the Los Angeles, Los Bambinos, and the Barba (also called Bermúdez) aquifers. Underlying these lavas is the Tiribí Formation, which includes a thick layer of lava that forms the La Libertad aquifer and is separated from the underlying Colima Formation by a tuff layer. The Colima Formation of lavas includes the two most important aquifers in the western Central Valley, Colima Superior and Colima Inferior, which are separated by tuff and ignimbrite layers that behave as aquitards. Thick lahars (mudflows) and alluvial deposits are present in the eastern part of the Virilla River basin, and have formed small local aquifers.

Recharge to the shallow aquifers (Barba, Los Bambinos, and La Libertad) is primarily by direct infiltration following precipitation, whereas for the deeper Colima aquifers, it is probably either from percolation from the upper aquifers through the pyroclast beds (8, 34), or by direct infiltration from precipitation in the eastern part of the Central Valley (35).

Annual precipitation in the Virilla River basin ranges from 1400 to 5200 mm, concentrated in the period ranging from May through November. It has been estimated that approximately 30 percent of the precipitation infiltrates and recharges the aquifers in this region (36), although groundwater recharge, especially in the upper part of the basin, is a rather complicated process. Average annual air temperatures range from 20 to 25°C, and only slight seasonal changes are observed. Land use in the area varies according to elevation: pastures and forests are common at elevations higher than 1600 m asl (Photo 1);

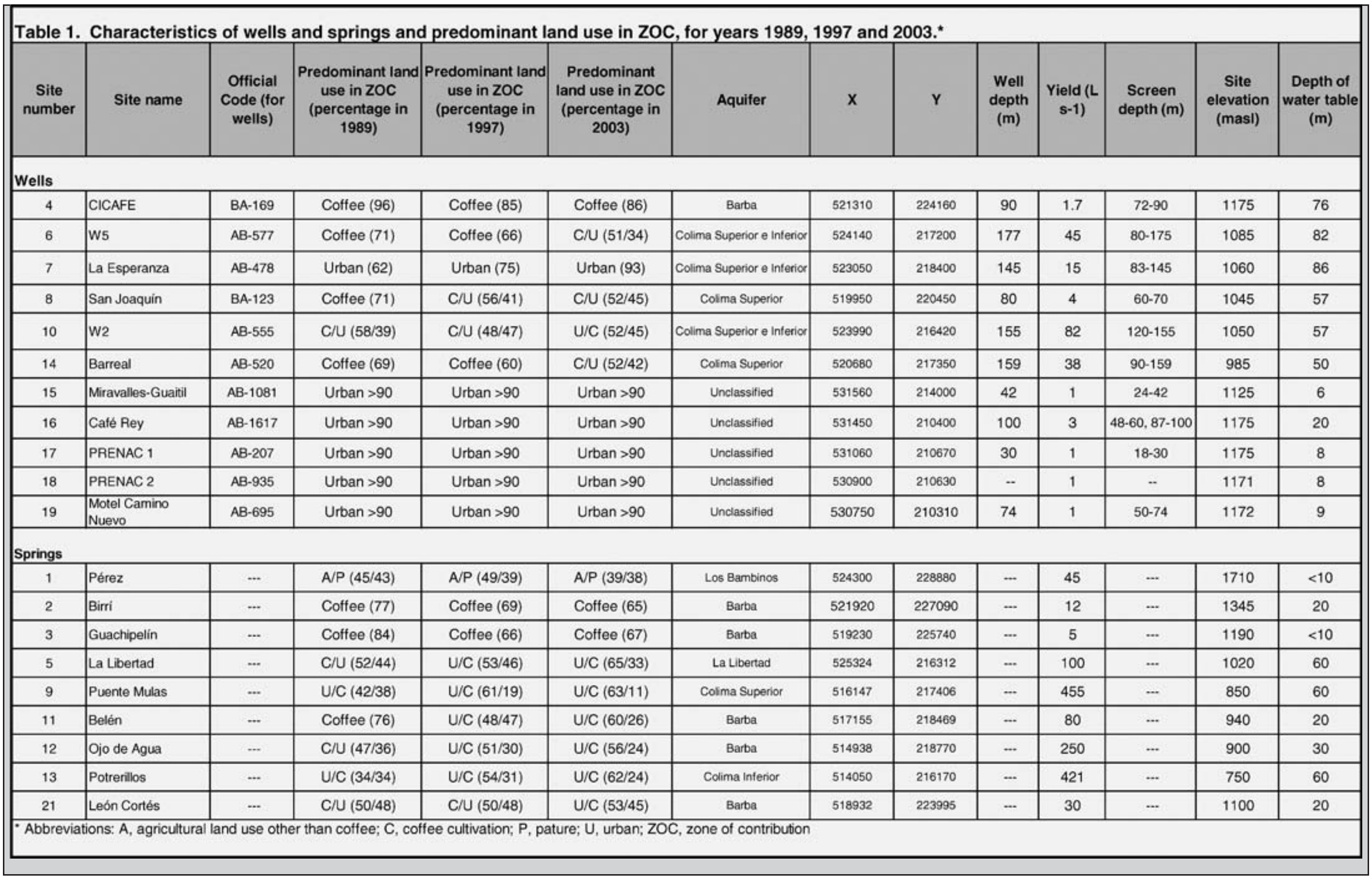

Table 1. Characteristics of wells and springs and predominant land use in ZOC, for years 1989, 1997 and 2003.*

Site number	Site name	Official Code (for wells)	Predominant land use in ZOC (percentage in 1989)	Predominant land use in ZOC (percentage in 1997)	Predominant land use in ZOC (percentage in 2003)	Aquifer	X	Y	Well depth (m)	Yield (L s-1)	Screen depth (m)	Site elevation (masl)	Depth of water table (m)
Wells													
4	CICAFE	BA-169	Coffee (96)	Coffee (85)	Coffee (86)	Barba	521310	224160	90	1.7	72-90	1175	76
6	W5	AB-577	Coffee (71)	Coffee (66)	C/U (51/34)	Colima Superior e Inferior	524140	217200	177	45	80-175	1085	82
7	La Esperanza	AB-478	Urban (62)	Urban (75)	Urban (93)	Colima Superior e Inferior	523050	218400	145	15	83-145	1060	86
8	San Joaquín	BA-123	Coffee (71)	C/U (56/41)	C/U (52/45)	Colima Superior	519950	220450	80	4	60-70	1045	57
10	W2	AB-555	C/U (58/39)	C/U (48/47)	U/C (52/45)	Colima Superior e Inferior	523990	216420	155	82	120-155	1050	57
14	Barreal	AB-520	Coffee (69)	Coffee (60)	C/U (52/42)	Colima Superior	520680	217350	159	38	90-159	985	50
15	Miravalles-Guaitil	AB-1081	Urban >90	Urban >90	Urban >90	Unclassified	531560	214000	42	1	24-42	1125	6
16	Café Rey	AB-1617	Urban >90	Urban >90	Urban >90	Unclassified	531450	210400	100	3	48-60, 87-100	1175	20
17	PRENAC 1	AB-207	Urban >90	Urban >90	Urban >90	Unclassified	531060	210670	30	1	18-30	1175	8
18	PRENAC 2	AB-935	Urban >90	Urban >90	Urban >90	Unclassified	530900	210630	--	1	--	1171	8
19	Motel Camino Nuevo	AB-695	Urban >90	Urban >90	Urban >90	Unclassified	530750	210310	74	1	50-74	1172	9
Springs													
1	Pérez	---	A/P (45/43)	A/P (49/39)	A/P (39/38)	Los Bambinos	524300	228880	---	45	---	1710	<10
2	Birrí	---	Coffee (77)	Coffee (69)	Coffee (65)	Barba	521920	227090	---	12	---	1345	20
3	Guachipelín	---	Coffee (84)	Coffee (66)	Coffee (67)	Barba	519230	225740	---	5	---	1190	<10
5	La Libertad	---	C/U (52/44)	U/C (53/46)	U/C (65/33)	La Libertad	525324	216312	---	100	---	1020	60
9	Puente Mulas	---	U/C (42/38)	U/C (61/19)	U/C (63/11)	Colima Superior	516147	217406	---	455	---	850	60
11	Belén	---	Coffee (76)	U/C (48/47)	U/C (60/26)	Barba	517155	218469	---	80	---	940	20
12	Ojo de Agua	---	C/U (47/36)	U/C (51/30)	U/C (56/24)	Barba	514938	218770	---	250	---	900	30
13	Potrerillos	---	U/C (34/34)	U/C (54/31)	U/C (62/24)	Colima Inferior	514050	216170	---	421	---	750	60
21	León Cortés	---	C/U (50/48)	C/U (50/48)	U/C (53/45)	Barba	518932	223995	---	30	---	1100	20

* Abbreviations: A, agricultural land use other than coffee; C, coffee cultivation; P, pature; U, urban; ZOC, zone of contribution

intensively managed coffee plantations, currently occupying approximately one-third of the basin, predominate at elevations between 1000 and 1600 m asl. Urban areas are located primarily on the flat areas, in the lowest part of the basin, between 700 and 900 m asl. Small networks of old sewers exist in urban centers and in some residential areas; however, pipelines usually collect and discharge sewage with little or no treatment into rivers. Most wastewater in the rest of the Central Valley is disposed of through septic tanks.

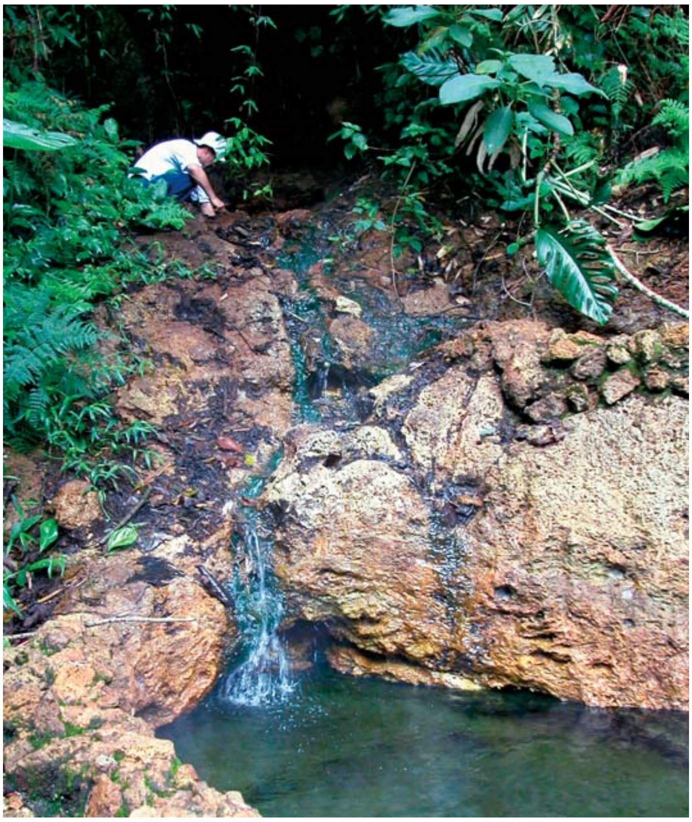

Photo 2 Sampling at one of the high elevation springs. Photo: J. Reynolds-Vargas.

MATERIALS AND METHODS

Nitrate data presented here correspond to results obtained by the first author during years 1988–1990 (9), and data collected by the Environmental Hydrology Laboratory from 1990 through 2004. In total, 9 springs and 11 wells were sampled from 4 to 17 y. Six sites located in densely urbanized localities were added to the sampling network in 1997. Although no long-term nitrate data are available for Site 19, results are included because isotopic analyses were also conducted in water extracted from this borehole. Water samples came from several aquifers within the system: Los Bambinos, Barba, La Libertad, Colima Superior, and Colima Inferior, and from groundwater deposits formed in unclassified lahars in the eastern part of the Virilla River basin. Sampling sites are located along a gradient from 750 to 1700 m asl (Photo 2).

Samples were collected in duplicate from springs and drinking water wells, kept refrigerated and taken to the laboratory, where they were analyzed within 24 hr. To remove stagnant water, all wells, but especially those that were not pumping at the time of sampling, were purged until chemical parameters (conductivity, pH, and temperature) were stabilized. Nitrate-N analyses were conducted by the Soils Laboratory of the School of Natural Resources, University of Michigan, from 1988 to 1990, and by the Environmental Hydrology Laboratory at Universidad Nacional from 1991 to 2004. Some of the analyses during years 1991, 1992, and 1994 were performed by the Costa Rican Institute for Water Works and Sewerage

(AyA). Results of nitrate analyses are expressed as nitrate-nitrogen (NO_3^{-1}-N).

Monthly precipitation and temperature data from several weather stations in the study area were provided by the National Meteorological Institute. Because there is not a significant temperature difference throughout the year, only precipitation data were correlated with nitrate concentrations in groundwater.

To obtain an isotopic characterization of nitrate in groundwater, $\delta^{15}N_{NO3}^{-}$ and $\delta^{18}O_{NO3}^{-}$ were determined in water from selected sites, and in potassium nitrate fertilizer, which is regularly used in coffee plantations. Isotopic analyses were conducted by the Hydroisotop Laboratory, in Freising, Germany; and by the Environmental Isotope Laboratory of the University of Waterloo, in Canada. The zone of contribution (ZOC) of each well and spring was defined using potentiometric hydrogeologic maps and traditional analytical procedures (37), on the basis of the type of aquifer, transmissivity, average steady-state pumping flow, and aquifer recharge. Land use on each ZOC for 1989 was determined using 1:10 000 maps (38). Land use in 1997 was determined using aerial photographs (39), and for 2003, using infrared aerial photographs (40). Human waste disposal methods were determined for the area within each ZOC using information and maps provided by municipal governments by the AyA.

The concentration of persistent mobile nitrate contaminant leached from agricultural soils was estimated by using a very approximate and simplified equation proposed by Foster and Hirata (10):

$$C_F = F * f_f * 100 * I^{-1}$$

where, C_F (mg L^{-1}) is the concentration of nitrate contaminant (mg L^{-1}, as NO_3^-), I (mm yr^{-1}) is the local infiltration due to excess rainfall, F (kg ha^{-1} yr^{-1}) is the total annual amount of applied fertilizer per unit area (as nitrate) (200 to 400 kg ha^{-1}), and f_f (dimensionless) is the proportion of contaminant leached into the subsurface.

The estimation was made considering three different scenarios of annual fertilizer application: 200, 300, and 400 kg ha^{-1} of nitrate (F) (41, 42), an f_f factor of 0.5 (11), and a recharge rate (I) of 600 mm yr^{-1} (30% of the total precipitation[1]).

Likewise, a semiquantitative estimation of the resultant nitrate concentration in groundwater was made for urban areas (C_u) using the equation:

$$C_u = (1000 * a * A * f_u)(0.36 * A * U + 10 * I)^{-1}$$

where a is the unit weight of NO_3^--N in excreta (2–4 kg cap^{-1} yr^{-1}), A (persons/ha) is the population density, I (mm yr^{-1}) is the rate of rainfall infiltration, U (L cap^{-1} d^{-1}) is the nonconsumptive portion of total water use), and f_u (dimensionless) is the proportion of excreted nitrogen leached into groundwater.

The nitrate potential concentrations in urban areas were estimated (C_u) considering three different average population densities (A): 50 inhabitants ha^{-1} (low-density housing), 80 hab ha^{-1} (mid-density), and 120 hab ha^{-1} (high-density) (29, 30); an annual recharge rate (I) of 100 mm considering the low permeability of land); an attenuation factor (f_u) of 0.5 (10); a nonconsumptive water use (U) of 125 L cap^{-1} d^{-1} (35); and a, the weight of nitrate in excreta of 4 kg cap^{-1} d^{-17} (10).

RESULTS

Characteristics of wells and springs sampled in the study area are shown in Table 1. On the basis of an analysis of land use in the ZOC of each well and spring in 1989, 1997, and 2003, the sites were divided into three groups (Table 2): *i)* sites located in predominantly agricultural areas, which in 2003 maintained more than 60 percent under coffee cultivation; *ii)* sites located in semiurban areas, which in 2003 had land use divided between agricultural and urban uses; and *iii)* sites with more than 75 percent of their ZOC under urban land use. Urban cover tended to increase in the majority of zones of contribution, whereas areas devoted to agriculture decreased over time (1989–2003).

Synthetic fertilizer (potassium nitrate) used in coffee plantations has an isotopic composition of 4.3‰ for δ^{15}N and 18.9 for δ^{18}O. Isotopic data of nitrate in groundwater are presented in Table 3. The result of δ^{15}N analysis for Site 1 was 3.6‰, which was considered the background isotopic value. For springs and wells primarily under agricultural influences, δ^{15}N ranges between 5.4 and 8.8‰, and δ^{18}O from 5.2 to 9.6‰; in semiurban areas δ^{15}N ranges between 5.6 and 9.4‰, and δ^{18}O from 2.8 to 8.05‰. In predominantly urban areas, δ^{15}N ranges from 8.0 to 20.7‰ and δ^{18}O from 4.7 to 13.2‰. Average δ^{15}N values tend to increase as land use changes from agricultural to urban.

Mean nitrate concentration at the highest elevation site (1710 m asl) is 0.54 mg L^{-1}. This value is considered as the background concentration. Average nitrate concentrations tend to increase following land use changes from agricultural (primarily coffee cultivation) to urban development, except in samples taken from aquifers underlying urban areas with sewerage systems (wells Miravalles-Guaitil, Café Rey, PRENAC 1, and PRENAC 2), which had lower nitrate concentrations. In general, springs tend to have higher average nitrate concentrations than wells: 4.6 mg L^{-1} and 2.6 mg L^{-1}, respectively.

No significant difference was found in nitrate concentrations in water from springs and wells in the Barba, Colima Superior, and Colima Inferior aquifers. The highest average value was observed in the Belén spring, where concentrations exceeded the maximum recommended value of 10 mg N L^{-1} on several occasions during the period of study. No significant correlation was found between precipitation amounts and nitrate concentrations in groundwater.

Long-term data analysis shows an increasing trend in nitrate concentrations, which is statistically significant ($p < 0.01$) in five sites, three of which were monitored more than 12 y: CICAFE well and Guachipelín spring, located in areas under intensive coffee cultivation, and Ojo de Agua spring (Fig. 3), which has approximately 50 percent of its ZOC in urban use. All three sites extract water from the Barba aquifer. The other two sites, which were monitored for only 5 y, are León Cortés spring, located in a semiurban area, and PRENAC II well, located in an urban area with sewerage systems. An extrapolation of the trends indicate that the recommended maximum concentration of 10 mg N L^{-1} will be reached in a period ranging from 10 to 40 y in all five sites.

The results of the estimation of nitrate derived from coffee plantations, using the formulas proposed by Foster and Hirata (1988) described in the previous section, under applications of 200, 300, and 400 kg ha^{-1} of nitrogen fertilizer were 3.9, 5.7, and 7.5 mg L^{-1} NO_3-N, respectively. Nitrate concentrations estimated in groundwater under different land occupation densities were: 8.2 mg L^{-1} NO_3-N for areas of low population density, 9.3 mg L^{-1} NO_3-N for areas with medium population density, and 10.0 mg L^{-1} NO_3-N for areas with high population density.

DISCUSSION

Impact of Land Use Changes on Groundwater Quality

The results of this investigation demonstrate that as a result of land use changes associated with an intensive use of on-site

Table 2. Waste disposal system in zone of contribution (ZOC) and nitrate concentration in wells and springs.

Site number	Site name	Waste disposal system in ZOC	Sampling years	N	Average NO_3-N concentration (mg/L) and standard deviation	Range NO_3-N concentration (mg L^{-1})
1	Pérez spring	Septic tank	1988–2001	68	0.5 (±0.4)	0.03–2.49
NO_3-N concentration in predominantly agricultural areas						
4	CICAFE well	Septic tank	1988–2001	68	2.3 (±1.0)	0.16–4.74
2	Birrí spring	Septic tank	1988–1997	49	0.7 (±0.3)	0.07–2.15
3	Guachipelín spring	Septic tank	1988–2001	62	3.0 (±1.1)	0.64–5.87
	Average				2.0	
NO_3-N concentration in semiurban areas						
6	W5 well	Septic tank	1990–2001	44	1.5 (±0.9)	0.63–4.74
14	Barreal well	Septic tank	1991–2001	31	4.6 (±2.0)	0.89–8.38
8	San Joaquín well	Septic tank	1990–2001	46	1.0 (±0.6)	0.30–3.16
10	W2 well	Septic tank	1990–2001	46	5.0 (±1.1)	1.58–7.91
21	León Cortés spring (Santa Bárbara)	Septic tank	1997–2001	17	6.3 (±0.6)	5.01–6.88
11	Belén spring (San Antonio)	Septic tank	1988–2004	78	7.9 (±2.5)	2.06–18.52
12	Ojo de Agua spring	Septic tank	1988–2004	81	4.9 (±1.5)	1.65–9.94
13	Potrerillos spring	Septic tank	1990–2001	9	1.8 (±0.3)	1.13–1.97
5	La Libertad spring	Septic tank	1990–2002	45	7.0 (±1.3)	4.74–12.42
9	Puente Mulas spring	Septic tank	1990–2004	46	5.8 (±0.9)	3.84–8.80
	Average				4.6	
NO_3-N concentration in urban areas						
7	La Esperanza well	Septic tank	1990–1999	25	4.3 (±1.8)	0.99–8.36
15	Miravalles-Guaitil well	Mains sewerage	1997–2001	19	1.9 (±1.0)	0.90–4.15
16	Café Rey well	Mains sewerage	1997–2001	19	0.8 (±1.2)	0.02–3.57
17	PRENAC 1 well	Mains sewerage	1997–2001	19	0.8 (±0.2)	0.59–1.24
18	PRENAC 2 well	Mains sewerage	1997–2001	17	1.8 (±0.5)	0.67–2.56
19	Motel Camino Nuevo well	Septic tank	1997	2	4.03	3.80–4.26
	Average				2.3	

sanitation systems, nitrate contamination will continue to increase in groundwater from the Central Valley in Costa Rica. Assuming a constant contaminant input to the groundwater, the projection of trends in nitrate concentrations indicate that in a few decades water will become unsuitable for drinking in five of the studied sites, most of which are being used as public water supply sources. It may be inevitable that intensive urbanization will continue to degrade groundwater quality if measures are not taken to control sources of pollution. Given the complexity of recharge processes, the continuous input of nitrogen from multiple sources and the slow transit times of groundwater, nitrate can persist in the aquifers for decades.

Changes in land use patterns from coffee plantations to urban residential areas either without sewerage systems or with inadequately installed and maintained septic tanks tend to increase the potential nitrate contaminant load into the subsurface in the recharge areas overlying the Barba, La Libertad, and Colima aquifers. Even in the deepest confined and semiconfined Colima aquifers the quality of water is likely to deteriorate as pollution loads continue to penetrate through the Barba Formation.

The highest concentrations of nitrate (>4 mg L^{-1} NO_3-N) were observed in urban and semiurban areas lacking primary sewage collection systems, whereas wells and springs located in agricultural areas—those planted primarily with coffee—show an average nitrate concentration of 2.0 mg L^{-1} NO_3-N. Although nitrate concentrations greater than 10 mg L^{-1} (as NO_3-N) were not encountered on a regular basis, the increasing

Table 3. Results of Isotopic analysis of nitrate in groundwater overlaid by agricultural, semiurban, and urban areas.

Site number	Site name	$\delta\ ^{15}N_{NO3}$ (April 1997)	$\delta\ ^{15}N_{NO3}$ (January 1998)	$\delta\ ^{15}N_{NO3}$ (June 1999)	$\delta\ ^{15}N_{NO3}$ (average)	$\delta\ ^{15}O_{NO3}$ (April 1997)	$\delta\ ^{15}O_{NO3}$ (January 1998)	$\delta\ ^{15}N_{NO3}$ (June 1999)	$\delta\ ^{18}O_{NO3}$ (average)
1	Pérez spring		3.6		3.6				
$\delta\ ^{15}N_{NO3}$ in predominantly agricultural areas									
4	CICAFE well		8.8		8.8		8.4		8.4
2	Birrí spring		5.8		5.8		5.2		5.2
3	Guachipelín spring			5.4	5.4			9.6	9.6
	Average				6.7				7.7
$\delta\ ^{15}N_{NO3}$ in semiurban areas									
6	W5 well								
14	El Barreal well	6.5	7.7		7.1	4.6	7.7		6.2
8	San Joaquín well								
10	W2 well	8.6	9.4	9.4	9.1	3.9	6.0	6.0	5.3
21	León Cortés spring		7.6		7.6		8.0		8.0
11	Belén spring	8.0	9.1		8.5	2.8	4.9		3.9
12	Ojo de Agua spring	6.0	6.2	8.5	6.9	3.4	5.6	7.8	5.6
13	Potrerillos spring	6.6	7.4		7.0	6.9	8.1		7.5
5	La Libertad spring	5.6	5.9		5.8	3.6	5.7		4.7
9	Puente Mulas spring	7.5	7.3		7.4	3.9	5.2		4.6
	Average				7.4				5.7
$\delta\ ^{15}N_{NO3}$ in urban areas									
7	La Esperanza well								
15	Miravalles-Guaitil well	8.0			8.0				
16	Café Rey well	20.7	9.4		15.0		13.2		13.2
17	PRENAC 1 well								
18	PRENAC 2 well								
19	Motel Camino Nuevo well	10.5	12.2		11.3	4.7	5.8		5.3
	Average				11.5				9.2

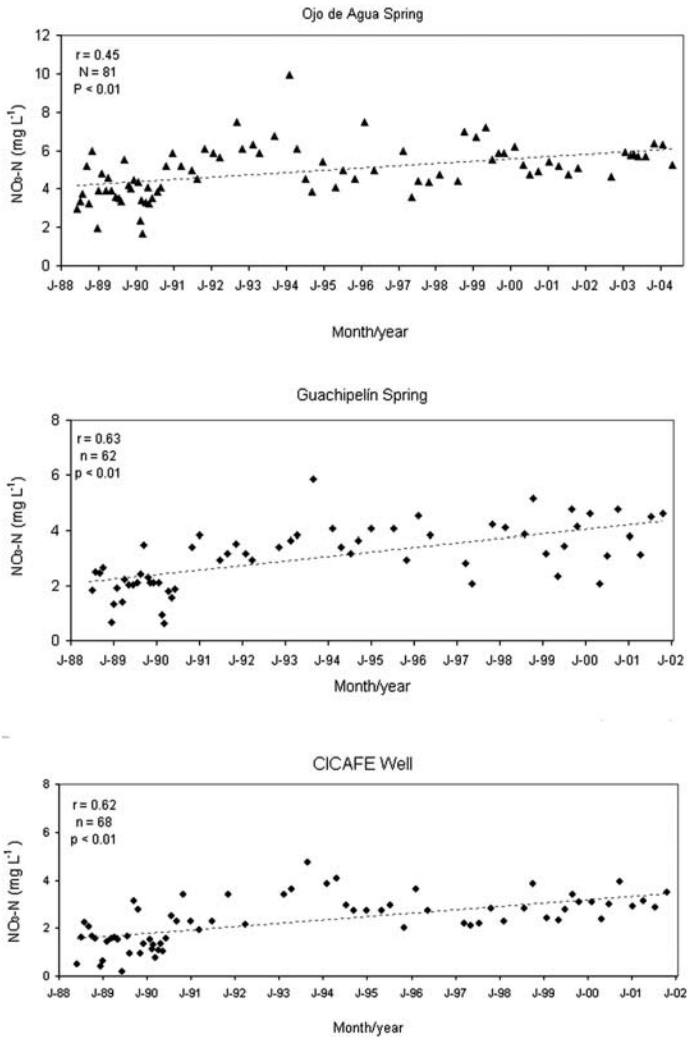

Figure 3. Trends in nitrate concentrations in Ojo de Agua and Guachipelín springs and CICIFE well.

trend found in several sampling sites is certainly a matter of concern. It is possible that the contaminant concentration increase observed in several wells and springs in the Central Valley is a result of changes in land use. Urbanization has indeed changed the patterns of recharge in the lower parts of the Central Valley, not only by reducing the permeability of the soil, but also by modifying the pathways taken by recharge and by introducing other recharge sources, which may also be adding other contaminants that are harmful to human health.

Although there are many uncertainties related to the estimation of nitrate leaching, it is evident that land use substitution processes from agricultural activity to housing without proper sewerage systems may cause an increase in the nitrate contaminant load of up to 40 percent. Nitrate concentrations will continue to rise beneath populated areas unless an integral approach to sanitation and groundwater resource management is implemented. This increase is occurring even though nitrate leaching processes may be attenuated to some extent by adsorption processes characteristic of volcanic soils.

On-site sanitation facilities are an inexpensive method for recovery and disposal of human waste, but these systems may also be an important cause of groundwater pollution. This is particularly relevant in a region such as the Central Valley, where the population is increasingly dependent on the underlying aquifers as sources of drinking water. As urbanization grows, nitrate may be considered only the first of several potential—not yet evaluated—contaminants that may be encountered in the future. Even the location of disposal sites for treated sewage effluents and the density of septic tanks allowed will require careful evaluation. Unfortunately, the presence of nitrate even at the semiconfined Colima aquifer suggests that the quality of all groundwater is likely to deteriorate even further, and that the upper layers of volcanic, fractured rocks are not sufficient to protect the deepest aquifers.

Application of Isotopic Techniques

Measurements of nitrogen and oxygen isotope ratios ($^{15}N/^{14}N$ and $^{18}O/^{16}O$) provided useful information about dominant sources of nitrate, which is prevalent in sewage effluents and agricultural fertilizers. It is evident that the most adequate way to determine the origin of nitrate in groundwater should include $\delta^{15}N$ analysis in nitrate combined with more conventional methods such as the study of land use patterns. When isotopic results are related to land use data in the area of influence, $\delta^{15}N_{NO3}{}^{-}$ seems to be a valid indicator of the source of contamination.

Multipoint or localized sources of nitrate consist primarily of septic tanks, whereas diffuse or widespread sources include inorganic nitrogen fertilizer applied to coffee plantations. All of these sources are likely to release nitrate into the soil. There is evidence that natural nitrate concentrations are relatively low in the soil solution and the contribution of nitrification processes in the soil is likely to be relatively small (5). For this reason, it is unlikely that natural soil organic nitrogen is significantly contributing to groundwater contamination in the study area.

Isotopic results in this study indicate that nitrate in groundwater in the Central Valley is derived mainly from two sources: nitrogen fertilizers in areas cultivated with coffee, and sewage in urban and semiurban areas. The samples from wells in urban areas have heavy isotopic values, ranging from 8 to 20.7‰ $\delta^{15}N_{\mathbf{NO3}}{}^{-}$, which is very near or greater than 10‰, and which is an indication of pollution by animal or sewage waste, although nitrate concentrations remain low (less than 2 mg N L^{-1}) in urban boreholes located in areas served by sewerage mains. In general, nitrate from urban areas show more enriched $\delta^{15}N$ values than nitrate from springs and wells in predominantly agricultural areas. Despite the attenuation due to the high precipitation and infiltration rates and to the slow rates of solute movement, the effect of increasing urbanization and of fertilizer application is becoming apparent in the groundwater.

The results of $\delta^{18}O_{NO3}{}^{-}$ analysis in groundwater are between 2.8 and 13.2‰, which are different from the results obtained from the $\delta^{18}O_{NO3}{}^{-}$ analysis of chemical fertilizer in this study (18.9‰) and that of other investigations (43), or from the results obtained for $\delta^{18}O_{NO3}{}^{-}$ in human and animal wastes by Amberger and Schmidt (26). Thus, a clear differentiation of nitrate from various sites could not be established on the basis of the $\delta^{18}O_{NO3}{}^{-}$ data. The data obtained in this study and those in the literature (25) suggest that $\delta^{18}O_{NO3}{}^{-}$ may not be the most adequate tracer for distinguishing between nitrate sources.

As land use is inevitably shifting toward increased urbanization, the density of septic tanks and the location of new disposal sites for treated sewage effluents should be carefully evaluated. Groundwater quality could remain degraded for a long time, and any changes in land use may not be reflected in groundwater quality for 5 to 15 y.

Protecting groundwater from further degradation requires not only scientific information and public awareness, but also political decisions accompanied by considerable economic investments in adequate wastewater disposal systems. Land use planning to orient urban growth is becoming an urgent need in the Central Valley, and more research is required for a full understanding of the mechanisms involved in groundwater contamination in this complex hydrogeologic system. Recommended urgent actions include continued monitoring and the definition of wellhead protection areas.

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