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Key Points:

- Four decades of land use change have increased groundwater nitrate concentrations in central Costa Rica
- Deeper aquifer units were characterized by low nitrate concentrations, whereas greater values were reported in the shallow unconfined unit
- Nitrogen and oxygen stable isotopes revealed unknown recharge mechanisms and nitrogen pollution sources in a tropical volcanic aquifer

Supporting Information:

Supporting Information may be found in the online version of this article.

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Nitrate Legacy in a Tropical and Complex Fractured Volcanic Aquifer System

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Abstract Nitrate legacy is affecting groundwater sources across the tropics. This study describes isotopic and ionic spatial trends across a tropical, fractured, volcanic multi-aquifer system in central Costa Rica in relation to land use change over four decades. Springs and wells (from 800 to 2,400 m asl) were sampled for NO_3^- and Cl^- concentrations, $\delta^{18}O_{water}$, $\delta^{15}N_{NO3}$, and $\delta^{18}O_{NO3}$. A Bayesian isotope mixing model was used to estimate potential source contributions to the nitrate legacy in groundwater. Land use change was evaluated using satellite imagery from 1979 to 2019. The lower nitrate concentrations (<1 mg/L NO_3^--N) were reported in headwater springs near protected forested areas, while greater concentrations (up to ~63 mg/L) were reported in wells (mid- and low-elevation sites in the unconfined unit) and low-elevation springs. High-elevation springs were characterized by low Cl^- and moderate NO_3^-/Cl^- ratios, indicating the potential influence of soil nitrogen (SN) inputs. Wells and low-elevation springs exhibited greater NO_3^-/Cl^- ratios and Cl^- concentrations above 100 μmol/L. Bayesian calculations suggest a mixture of sewage (domestic septic tanks), SN (forested recharge areas), and chemical fertilizers (coffee plantations), as a direct result of abrupt land use change in the last 40 years. Our results confirm the incipient trend in increasing groundwater nitrogen and highlight the urgent need for a multi-municipal plan to transition from domestic septic tanks to regional sewage treatment and sustainable agricultural practices to prevent future groundwater quality degradation effectively.

Plain Language Summary This study analyzed different nitrate sources in a complex tropical groundwater system and how they were affected by changes in land use over the last decades. In general, high-elevation areas near protected forests are represented by lower nitrate levels, while mid- and low-elevations areas exhibited greater nitrate and chloride concentrations. Our results suggest that groundwater nitrate reflects a legacy mixture of sewage (domestic septic tanks), soil nitrogen (forested recharge areas), and chemical fertilizers (coffee plantations), as a direct result of abrupt land use change in the last 40 years. The identified nitrate groundwater legacy in the Central Valley of Costa Rica, evidenced by unprecedented decadal nitrate isotope data, could serve as a valid example of the potential impact of abrupt urbanization growth across the wet tropics.

1. Introduction

Exponential population growth and fast expansion of urban centers (inland and coastal cities), crop areas, and industrial sectors in past decades have increased nitrogen loadings to surface waters and groundwater reservoirs across the globe (Galloway et al., 2004; Houlton et al., 2019; Kanter, 2018). This nutrient mobilization is affecting the biochemical functioning of natural-urban coupled systems (Collins et al., 2010; Lorenz & Lal, 2009; Müller et al., 2020). In turn, this can lead to the eutrophication of aquatic ecosystems (e.g., rivers, lakes) and consequently, a reduction of their biodiversity, and represents a public health concern since high nitrate levels in drinking water can result in methemoglobinemia, gastric cancer, and thyroid disorders (Gomes et al., 2023; Kanter et al., 2020; Matiatos et al., 2022).

Identifying the multiple nitrogen sources (i.e., precipitation, chemical fertilizers (CF), soil nitrogen (SN), manure, and sewage lixiviate) and mixing processes between point and non-point sources remains a fundamental environmental challenge in groundwater nitrate studies (Carrey et al., 2021; Jung et al., 2023). Nitrogen concentrations are also controlled by the co-existence of numerous biogeochemical processes (e.g., fixation, nitrification,

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and denitrification, among others) (Kendall, 1998; Qin et al., 2020; Reynolds-Vargas et al., 2006; Zhang, Shi, et al., 2018), which can be difficult to disentangle in a groundwater matrix. In this regard, isotope techniques represent a consolidated tool for determining potential nitrogen sources in surface and groundwater systems and evaluating the biogeochemical transformations in the aquatic environment (Chang et al., 2022; Halder et al., 2022; Harris et al., 2022; Li et al., 2022; Sigler et al., 2022; Zaryab et al., 2022). Environmental isotopes (e.g., ^{15}N, ^{18}O, ^{34}S, ^{11}B, ^{87}Sr) in combination with chemical, hydrometric, and GIS information offer novel opportunities for the understanding of nitrogen legacy pollution, source identification, and the efficiency of mitigation and conservation practices (Fenech et al., 2012; Rivett et al., 2008).

In recent years, Bayesian isotope mixing models have been used in ecology, geology, hydrology, and other fields to estimate the contributions of different sources to a complex mixture (Birkel et al., 2021; Jasra et al., 2006; Kadoya et al., 2012; Xue et al., 2012; Zhang et al., 2020). This technique offers some advantages such as (a) the incorporation of prior information about the sources and their isotopic compositions, which can improve the accuracy of the estimates, particularly when there is limited data available; (b) these models can handle mixtures with multiple sources, even when the isotopic signatures of the sources are similar; and (c) provide estimates of uncertainty, which can be useful for interpreting the results and making decisions. Similarly, this modeling approach has limitations, such as (a) the accuracy of the estimates depends on the accuracy of the isotopic data for the sources and the assumptions made about their isotopic variability; (b) isotope mixing models are based on linear mixing models, which may not be appropriate for some types of mixtures that have non-linear relationships between the sources and the mixture; (c) the results can be sensitive to the choice of priors, particularly when the data are limited; and (d) these models can be complex and require technical expertise to implement and interpret (Correa et al., 2019; Moore & Semmens, 2008; Parnell et al., 2010; Semmens et al., 2009; Stock et al., 2018; Zhang, Zhi, et al., 2018).

In Central America, groundwater systems are dominated by highly productive aquifers (Ramírez-Chavarría and Alfaro (2002); Ballestero et al., 2007; Miller et al., 2012). Across this region, volcanic soils are characterized by high infiltration capacity (13–55 cm/month; Araguas-Araguas et al., 1994) and permeability, yielding large recharge rates of up to 1,605 mm/yr in complex and fractured volcanic aquifers of central Costa Rica (Sánchez-Murillo et al., 2022). Precisely, recent apparent groundwater age estimations and spatial hydrochemical trends across the northern slope of the Central Valley of Costa Rica (Madrigal-Solís et al., 2022; Sánchez-Murillo et al., 2022) revealed the existence of shallow (younger) and deeper (older) groundwater flow paths within this multi-aquifer volcanic system. Yet, historical nitrate increasing trends (Reynolds-Vargas et al., 2006) and the large degree of vertical and horizontal hydrogeological complexity reinforces the need to understand the key factors controlling natural and anthropogenic nutrient inputs and legacy transformations across this vital drinking water source for >1 million people in central Costa Rica.

Based on the early evidence of highly concerning groundwater nitrogen trends (Foster et al., 2002; Reynolds-Vargas et al., 2006), the main objective of this study is to understand the origin and spatial distribution of nitrogen sources of a tropical, volcanic, and fractured system of central Costa Rica. We combined $\delta^{15}N_{NO3}$, $\delta^{18}O_{NO3}$, $\delta^{18}O_{water}$, ion concentrations in a Bayesian mixing model framework to estimate endmember contributions (i.e., precipitation, CF, forested soils, manure, and dairy farming lixiviates, and residential sewage) to the overall nitrate legacy concentration in groundwater (i.e., springs and wells) across an altitudinal range (~800–2,400 m asl). We hypothesize that land use change over the last 40 years is mainly responsible for the existence of relatively high groundwater nitrate concentrations. Our results provide new insights into the inherent complexity of mixing processes across one of the most important water reservoirs for drinking water supply in central Costa Rica. This information could also delineate a potential route to reduce nitrate concentration by implementing strategic water management and urban planning in similar tropical and volcanic regions of Mesoamerica.

2. Study Area

The study area corresponds to the Barva-Colima multi-aquifer system (BCS) (~275 km^2; See Sánchez-Murillo et al., 2022 for detailed hydrogeological descriptions), on the northern slope of the Virilla River watershed (Figures 1a and 1b). This aquifer is located across the main urban center of Costa Rica with approximately 53% (2,268,248 inhabitants) of the country's population (Guillén Montero et al., 2021). Annual precipitation ranges from nearly 2,500 to 4,000 mm in the urban center and high-elevation recharge areas (Sánchez-Murillo et al., 2016; Sánchez-Gutiérrez, Benavides-Benavides, et al., 2020; Sánchez-Gutiérrez, Mena-Rivera, 2020), respectively.

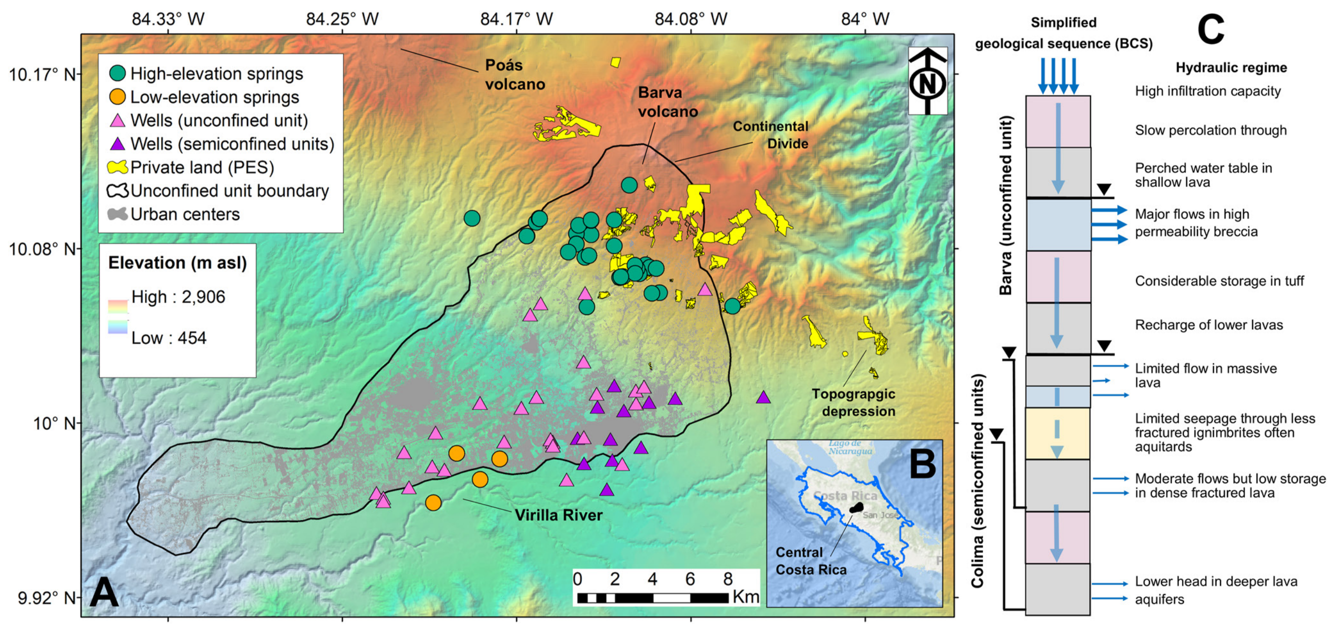

Figure 1. (a) The study area showing high and low elevation springs (dots) and wells (triangles) sampling sites across an elevation gradient from ~800 to 2,400 m asl in central Costa Rica. The black polygon denotes the best boundary limit of the Barva aquifer unit (Reynolds-Vargas & Fraile, 2009). Urban centers are represented by gray-shaded areas. Yellow polygons denote private protected land under the national Payment for Environmental Services scheme (PES). (b) The inset shows a regional overview of the study area in central Costa Rica. Vertical panel (c) shows a simplified geological sequence and hydraulic regime modified after Darling et al. (1989) and focuses on the main (BCS) formations: Barva, Upper, and Lower Colima.

Roughly 20% of total annual precipitation is recharged above 1,500 m asl (Sánchez-Murillo et al., 2022). Geological formations comprise highly fractured and brecciated material of the Central Volcanic Range in the headwaters (>1,500–2,906 m asl), mainly due to the activity of the Barva volcano during the Quaternary period (Miller et al., 2012; Reynolds-Vargas et al., 2006; Salas-Navarro et al. (2018); Sánchez-Murillo et al., 2016). The BCS is divided into two important aquifers: Barva and Colima. Among its four members, the Barva formation has a shallow unconfined aquifer unit, and the Colima aquifer is subdivided into two aquifers: Upper Colima (semiconfined) and Lower Colima (confined). The basements of both aquifers are constituted of low-permeability tuffs that allow water accumulation in the upper layers, being of great importance for the water supply to central Costa Rica (Figure 1c).

3. Methods

3.1. Sample Collection

Wells ($N = 53$) and springs ($N = 50$) were sampled (September 2019) for nitrate and chloride analysis (as NO_3^-N and Cl^- in mg/L) across the BCS (Figure 1a). The spatial pattern (in nitrate concentrations) was used to delineate the sampling sites (from high to low-elevation and covering the entire groundwater nitrate concentration range) for water ($\delta^{18}O$ and $\delta^{2}H$ in ‰, $N = 90$; 2019–2020) and nitrate ($\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- in ‰, $N = 35$) stable isotopes. Two sampling campaigns were conducted for $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- between October 2019 and June 2020. In total, 35 samples were collected (~800–2,400 m asl). Spring samples were collected from high and low-elevation sites representing the shallow Barva aquifer ($N = 6$). The number of springs sampled is limited due to the low prevalence of such systems, representing a clear high to low-elevation connectivity. Groundwater samples were collected in production wells representing the Barva and Colima aquifer units and the elevation range. Endmembers (as liquids) were grouped into four categories: (a) fertilizers (i.e., potassium, magnesium, ammonium, and calcium nitrate salts commonly used on coffee plantations; $N = 4$) ($Ca[NO_3]_2$, $Mg[NO_3]_2$, KNO_3, and NH_4NO_3), (b) soils (i.e., soil water extracts from west and east high-elevation forested headwaters; $N = 2$), (c) manure and sewage (i.e., septic tanks, dairy farms, and wastewater treatment plant affluents; $N = 4$), and (d) precipitation ($N = 156$, 2018–2020; Villalobos-Forbes et al., 2021). Fertilizer dissolutions were prepared in 100 mL volumetric flasks with a nitrate concentration of 10 mg/L in agreement with the maximum permissible nitrate concentration in drinking water for Costa Rica. All spring and groundwater samples and endmembers were immediately filtered after collection using 0.20 μm PTFE and/or PVDF filter into 40 mL amber glass vials with 0.2 mL of Suprapur ®hydrochloridic acid added for preservation. Precipitation samples were collected using a bulk precipitation sampler. Samples were filtered using 0.45 μm polytetrafluorethylene (PTFE) syringe membranes. One portion of the sample was transferred into polyethylene bottles and stored at dark and cool conditions (5°C) until ion analysis. Another portion of the precipitation sample (30 mL) was stored at dark and frozen conditions (−10°C) until shipment for nitrate isotope analysis to the Stable Isotope Hydrology Laboratory at the International Atomic Energy Agency (IAEA), Vienna, Austria. The datasets presented in this study are accessible at HydroShare, http://www.hydroshare.org/resource/a356a513daa34c58ba3c11bb20d2e3ea and in Tables S1–S4.

3.2. Nitrate and Chloride Analysis

Nitrate and chloride concentrations were determined using ion chromatography (Thermo Scientific ICS-5000+, CA, USA) with a detection limit of 0.33 and 0.20 mg/L, respectively. Blanks and recovery standards were included in each sample batch to ensure the quality of the analysis. Nitrate and chloride NIST (National Institute of Standards and Technology) traceable standard (1,000 mg/L) (*Trace*CERT®; SigmaAldrich, USA) were used for calibration and recovery procedures. Samples were filtered in the field using 0.20 μm PTFE and/or PVDF (polyvinylidene fluoride) filters into 5 mL HDPE (High-Density Polyethylene) pre-cleaned poly vials. Samples were transported in a cooler and analyzed within the first 24 hr after collection.

3.3. Water Stable Isotopes Analysis

Samples were collected and stored at 5°C in 50 mL HDPE bottles with no headspace and plastic inserts to avoid evaporation. Samples were analyzed at the Stable Isotopes Research Group laboratory at the Universidad Nacional (Heredia, Costa Rica) using an IWA-45EP water analyzer (Los Gatos Research, Inc., California, USA) with a precision of ±0.5‰ for δ^2H and ±0.1‰ for $\delta^{18}O$ (1σ; 8 injections). Calibrated secondary standards MTW (Moscow, Idaho tap water) ($\delta^2H = -130.3$ ‰, $\delta^{18}O = -16.7$‰), USGS45 ($\delta^2H = -10.3$‰, $\delta^{18}O = -2.2$‰), and CAS (commercial bottled water) ($\delta^2H = -64.3$ ‰, $\delta^{18}O = -8.3$‰) were used to normalize the results as well as to assess the quality and drift control procedures. $^{18}O/^{16}O$ and $^2H/^1H$ ratios are presented in delta notation δ (‰), relative to the VSMOW-SLAP scale.

3.4. Nitrate Stable Isotope Analysis

Nitrate stable isotope ($\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in ‰) analysis was conducted by Beta Analytic Testing Laboratory (Miami, Florida, USA). Samples were analyzed by chemical reduction of nitrate to nitrous oxide followed by continuous flow Isotope Ratio Mass Spectrometry (Altabet et al., 2019; Foreman et al., 2016). Each reduced sample was loaded into an auto-sampler which delivered sample gas to a Thermo Scientific Gas Bench II equipped with a denitrification kit. Each sample was run on a continuous flow Delta V with 10 pulses of reference N_2O gas with a standard deviation of <0.1‰ for $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$. This laboratory reference gas was standardized to USGS-32, USGS-34, and USGS-35 (Coplen, 2018). The nitrate isotope method uncertainty was ±2‰ (1σ) for $\delta^{18}O\text{-}NO_3^-$ and ±0.5‰ (1*σ*) for $\delta^{15}N\text{-}NO_3^-$.

Rainfall samples were analyzed by the Stable Isotope Hydrology Laboratory (IAEA). This laboratory uses a Titanium Ti (III) reduction method, which involves a one-step chemical conversion employing $TiCl_3$ to reduce nitrates to N_2O gas in septum sample vials (Altabet et al., 2019). The N_2O headspace was measured for ^{15}N and ^{18}O by coupling with a continuous-flow isotope-ratio mass spectrometer (IRMS, Isoprime 100) and a trace gas N_2O purification device. The analytical uncertainties were ±0.2‰ and ±0.4‰ for $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$, respectively. The standards used for the analysis were USGS34, USGS35, and IAEA-NO3. More details are described by Villalobos-Forbes et al. (2021).

3.5. Mixing Bayesian Model

We adapted the stable isotope mixing model from the R package *Simmr* (Parnell & Inger, 2016) to partition relative nitrate source contributions to groundwater using a Bayesian statistical framework based on a Gaussian likelihood. Four endmembers were selected: (a) fertilizers, (b) soils, (c) manure and sewage, and (d) precipitation. Endmembers isotope values are included in Table S2. The model requires three sets of input data as a minimum to determine the endmembers' contribution to groundwater nitrate. We included: (a) $\delta^{15}N$ and $\delta^{18}O$ from wells and springs (known as the mixtures; two sampling campaigns), (b) mean $\delta^{15}N$ and $\delta^{18}O$ for the endmembers, and (c) standard deviations of $\delta^{15}N$ and $\delta^{18}O$ for the endmembers. Springs were treated as a single group due to the low sample number. *Simmr* was implemented with 100,000 iterations discarding the first 10,000. No prior information was used, resulting in an equal likelihood of all sources (Gokool et al., 2018). The estimated nitrate source contribution to the groundwater mixture (springs and wells) was determined using a Markov Chain Monte Carlo (MCMC) function (Brooks, 1998) to repeatedly estimate the proportions of the various sources in the mixture and determine the values which best fit the mixture data (Parnell & Inger, 2016). Gelman-Rubin diagnostic (Gelman & Rubin, 1992) was performed to test model convergence using $\delta^{15}N$ and $\delta^{18}O$ values. The Gelman–Rubin diagnostic evaluates MCMC convergence by analyzing the difference between multiple Markov chains. Overall, all selected runs exhibited good model convergences (Gelman-Rubin value equal 1). Median (50% quantile) source water contributions from the posterior parameter distribution were used for practical comparisons. Historical nitrogen isotope values (1990–2004) (Reynolds-Vargas et al., 2006) were evaluated to estimate the nitrate groundwater source legacy evolution.

3.6. Land Use

Based on the suggested boundary of the Barva aquifer (unconfined unit) (Reynolds-Vargas & Fraile, 2009) (Figure 1a), we conducted a spatial analysis to understand the past (1979) and most recent (2019) land use conversion potentially driving nitrate spatial variations in groundwater. Satellite images were obtained from the Land Viewer (www.lv.eosda.com) and United States Geological Survey (USGS, 2022; https://earthexplorer.usgs.gov/) servers. Images with cloud coverage of less than 30% and without radiometric or radiance alterations in their pixels were selected for post-processing. Atmospheric corrections of the bands of interest used the Semi-Automatic Classification (SCP) tool in QGIS (2009). Land use was classified with the Maximum Likelihood algorithm, which best resembles the real distribution of the digital numbers in each category. The final raster was converted to a vector, where a polygonal generalization and simplification were applied. This process consists of obtaining a product in vector format that allows for minimizing the impulse noise, and, therefore, reducing or eliminating some incorrect pixels. We also calculated the area (in %) of each classification. More details are described by Sánchez-Murillo et al. (2022).

4. Results

The enigmatic high vertical and spatial complexity of the BCS has been reported by multiple studies (BGS, 1988; Arredondo Li & Soto, 2007; Madrigal-Solís et al., 2017, 2022; Miller et al., 2012; Ramírez & Alfaro, 2002; Ramírez-Chavarría, 2014; Reynolds-Vargas et al., 2006; Reynolds & Fraile (2009); Sánchez-Murillo et al., 2016, 2017, 2022). Our study analyzes the isotopic (water and nitrate) and ionic (nitrate and chloride) spatial patterns across this multi-aquifer system to provide modern insights into the legacy effects of the abrupt land use change and groundwater quality evolution during the last 40 years, in conjunction with a population density change from 46 to 102 inhabitants per km^2.

4.1. Nitrate Spatial Variations in Springs and Wells and Water Quality Limits

Spatial variation in groundwater NO_3^- (mg/L), in spring and well samples (from the Barva unconfined aquifer unit; Figure 1c) ranged from 0.70 (high elevation springs; >1,700 m asl) mg/L to 52.06 mg/L (lower elevation spring; ~800 m asl), and from 0.73 mg/L (upper semiconfined aquifer; ~1,225 m asl) to 63.0 mg/L (shallow unconfined aquifer unit; 1,050 m asl), respectively (Figure 2). In general, lower nitrate concentrations were reported in the upper basin area (2.5 ± 2.5 mg/L) (headwater springs near a national park sector and PES-protected forested areas; Pagiola, 2008), while greater concentrations were systematically reported in shallow wells (mid- and low-elevation wells in the unconfined unit) (18.5 ± 13.4 mg/L) and low-elevation springs (30.9 ± 15.7 mg/L) (Figure 2). Deeper semi-confined units exhibited lower nitrate concentrations (4.0 ± 3.5 mg/L).

The World Health Organization recommends a maximum admissible nitrate value of 50 mg/L in drinking water (WHO, 2017). The Costa Rican regulation for human water consumption suggests an alert and maximum admissible

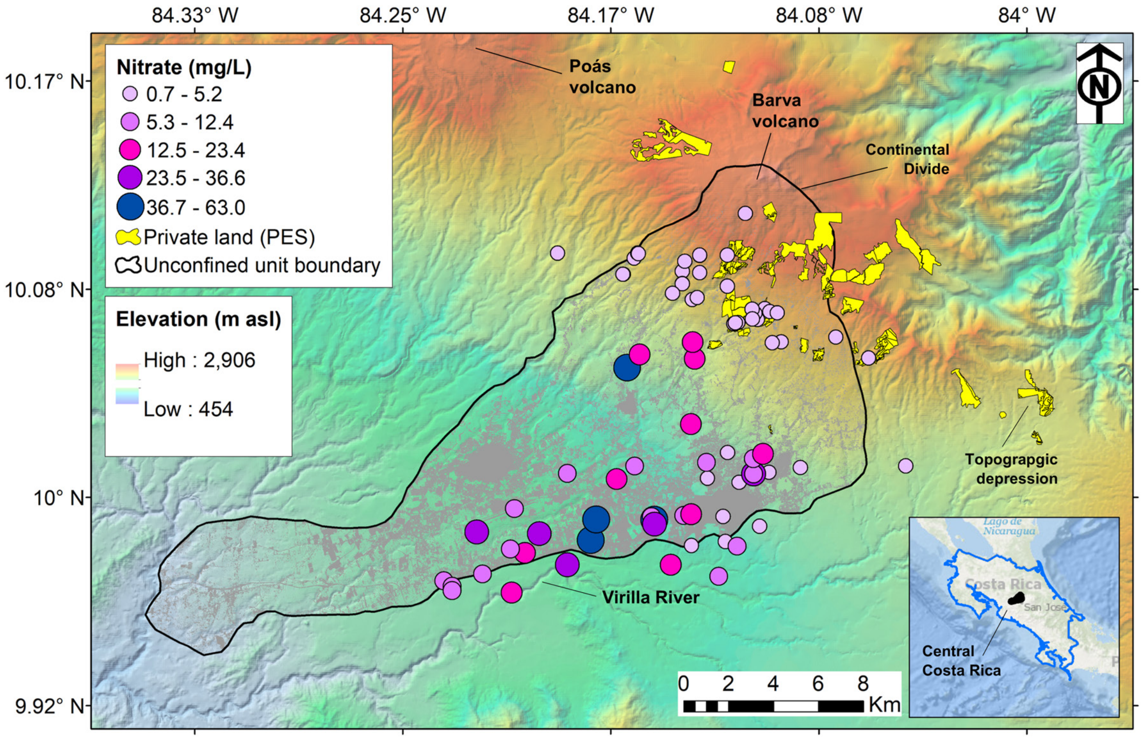

Figure 2. Nitrate spatial variability (mg/L) (color-coded) across the study area. Gray-shaded areas denote urban centers. Other study area details are described in Figure 1. The inset shows a regional overview of the study area in central Costa Rica.

value of 25 mg/L and 50 mg/L (MINSA, 2015), respectively. In this study, 10 samples (9.2%) (mid-to-low elevation) reported values above 25 mg/L, 23 samples (21.1%) (mid-to-high elevation) resulted in values between 10 and 25 mg/L, and 76 samples (69.7%) (mainly in high elevations and deeper wells) were below 10 mg/L. Overall, nitrate concentrations across the BCS are greater than previously reported in rural watersheds, protected areas, or highly altered coastal aquifers of Costa Rica (Jovanelly et al., 2020; Hernández-Alpízar & Mora-Molina, 2022; Sánchez-Gutiérrez, Benavides-Benavides, et al., 2020; Sánchez-Gutiérrez, Mena-Rivera, 2020). In addition, our results agree with the increasing nitrate trends reported during the last three decades (Madrigal-Solís et al., 2017; Reynolds-Vargas et al., 2006; Reynolds-Vargas & Richter, 1995) in central Costa Rica with NO_3^-N values ranging from 0.1 (high elevation) up to 18.5 mg/L (lowland) (1988–2004).

4.2. Isotopic and Ionic Compositions

Nitrate concentrations in low-elevation springs and several unconfined wells align with known isotope compositions in the Barva formation (Salas-Navarro et al., 2018; Sánchez-Murillo et al., 2016, 2017, 2022). In Figure 3, these samples are within $\delta^{18}O$ values of −8.0‰ and −9.5‰. In this multi-aquifer system, the Barva aquifer has been characterized by $\delta^{18}O$ median values near −9.0‰, relatively high tritium, and younger water age (<40 years; Sánchez-Murillo et al., 2022). Most high-elevation springs (green circles in Figure 3) exhibit similar depleted $\delta^{18}O$ compositions with lower nitrate concentrations. A group of high-elevation springs resulted in more depleted $\delta^{18}O$ compositions (~−11‰), which may indicate a different groundwater origin from the Poás aquifer located to the west of the BCS. However, the boundary limits between the Barva and Poás aquifers are still unclear (Hernández Ugalde, 2022; Reynolds-Vargas & Fraile, 2002; Vargas & Aguilar, 2011). Well samples from the deeper semiconfined Colima aquifer units were characterized by low nitrate concentrations and more enriched compositions. The Colima system has been characterized by low tritium, enriched $\delta^{18}O$ values, and older groundwater age (>60 years; Foster et al., 2002; Sánchez-Murillo et al., 2022). The isotopic difference between the Barva and Colima ayesianns will be further discussed in Section 5. The spatial $\delta^{18}O$ pattern is provided in Figure S1 in Supporting Information S1. In general, depleted compositions are observed in the north-western portion of the basin, whereas enriched compositions are observed toward the eastern domain. These patterns have

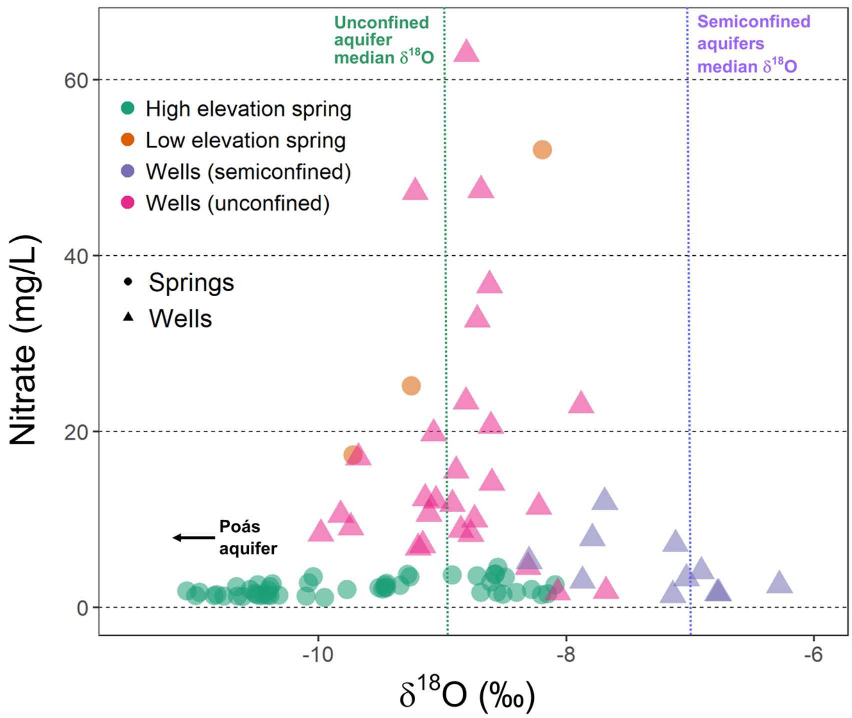

Figure 3. Dual plot between nitrate concentration (mg/L) and $\delta^{18}O$ (‰) in springs (low and high elevation) and wells (unconfined and semiconfined units) across the BCS. Color-code dashed lines denote the long-term median values within the Barva (unconfined) and Colima (semiconfined) units.

been previously documented in north-central Costa Rica (Sánchez-Murillo & Birkel, 2016; Sánchez-Murillo et al., 2017, 2022), and are also reflected in the isotope separation of the Barva and Colima aquifer formations.

Endmember associations between NO_3^-/Cl^- molar ratios and chloride concentration (μmol/L) (Figure S2 in Supporting Information S1) across the BCS are shown in Figure 4. High-elevation springs are characterized by low Cl^- and moderate NO_3^-/Cl^- molar ratios, indicating the potential influence of SN inputs. The headwaters are characterized by secondary protected forests (~80–100 years old) with high infiltration capacity, near saturation conditions throughout the year, short mean residence times, large carbon transport (Mayer-Anhalt et al., 2022; Sánchez-Murillo et al., 2019), and relatively low Cl^- (Madrigal-Solís et al., 2017). Wells and low-elevation springs, mainly representing the shallow unconfined aquifer unit, exhibited greater NO_3^-/Cl^- molar ratios and Cl^- above 100 μmol/L (3.5 mg/L). NO_3^-/Cl^- molar ratios also show a decreasing pattern with greater Cl^- values (>100 μmol/L). Typically, manure and sewage have a low NO_3^-/Cl^- ratio and high Cl^- concentration, whereas agricultural inputs are represented by a high NO_3^-/Cl^- ratio and low Cl^- concentration. In contrast, soil lixiviates are characterized by a low to moderate NO_3^-/Cl^- ratio and low Cl^- concentration (Huang et al., 2022; Jung et al., 2023; Weitzmann et al., 2021; Zhang et al., 2022). In general, low Cl^- (<2.8 mg/L) was consistently reported in high-elevation springs and in the deeper semi-confined aquifers, whereas greater values (up to 31.4 mg/L) were found in the upper unconfined aquifer unit and low elevation springs (Figure S2 in Supporting Information S1).

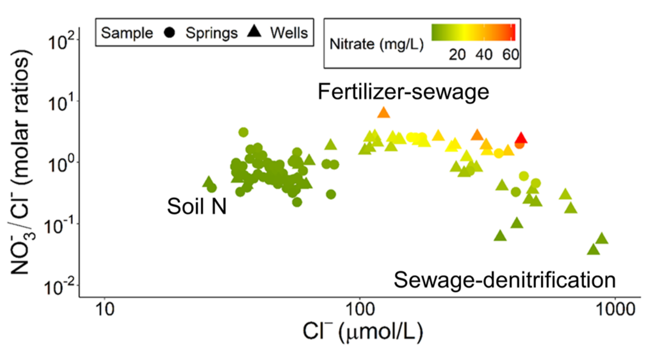

Figure 4. NO_3^-/Cl^- molar ratio and chloride concentration (μmol) in springs and wells (symbol coded) across the BCS. Nitrate concentrations are color-coded.

4.3. Evaluation of Nitrate Endmember Contributions Through Bayesian Mixing Modeling

In our study, springs and wells samples are mainly circumscribed within the isotopic domains of SN, manure, and sewage. Figure 5 shows the dual isotope diagram for $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- in groundwater (wells and springs) samples and four main endmember groups. Previously reported groundwater

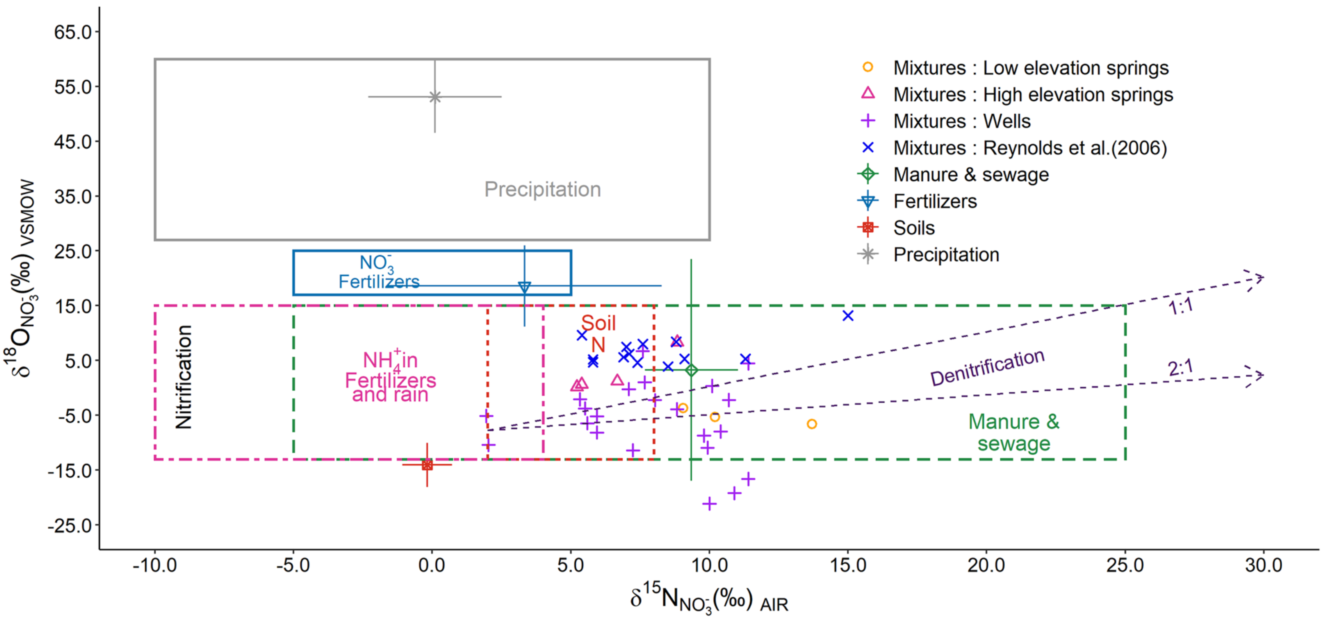

Figure 5. Dual isotope diagram of nitrate (δ^{15}N-NO_3^- vs. δ^{18}O-NO_3^-) in low and high-elevation springs (empty orange dots and pink triangles, respectively) and wells (purple crosses). Color-coded endmember domains were adapted from Kendall (1998), Kendall et al. (2007), and Xue et al. (2009). Historical values (blue crosses) from Reynolds-Vargas et al. (2006) are included as a reference. This data set was composed of three and five high- and low-elevation springs, and four low-elevation wells.

samples (springs and wells) from the study are included as a reference (Reynolds-Vargas et al., 2006). Overall, our endmember groups are distributed within previously known isotope domains (i.e., precipitation, fertilizers, soils, manure, and sewage) (Kendall, 1998, 2007; Xue et al., 2009). Across the BCS, springs and wells δ^{15}N-NO_3^- ranged from +1.95 ‰ to +13.7 ‰, with a mean of 8.1 ± 2.8‰, whereas δ^{18}O-NO_3^- ranged from −21.1 ‰ to +8.4 ‰, with a mean of −5.0 ± 6.9‰ (Figure 5). The values reported by Reynolds-Vargas et al. (2006) exhibited more enriched δ^{18}O-NO_3^- (−5 to +15 ‰) values within a similar δ^{15}N-NO_3^- range (+5 to +15 ‰).

Bayesian mixing estimations (Figures 6a–6c) revealed that manure and sewage are the predominant nitrogen contributors to nitrate for springs (low- and high-elevation) and wells, with mean proportions of 44.8 ± 23.8% and 69.4 ± 11.2%, respectively (Figures 6a and 6b). In high-elevation springs, manure from dairy farms may be responsible for this large contribution. Commonly, waste waters from dairy farms are directly discharged to pasture areas twice a day with no treatment. In the lowland urban areas, the large sewage contribution may be potentially related to the lack of a regional wastewater treatment system, where outdated septic tanks area a common feature. Soil nitrogen inputs accounted for 33.5% ± 20.5% and 21.7% ± 11.4%, in springs and wells,

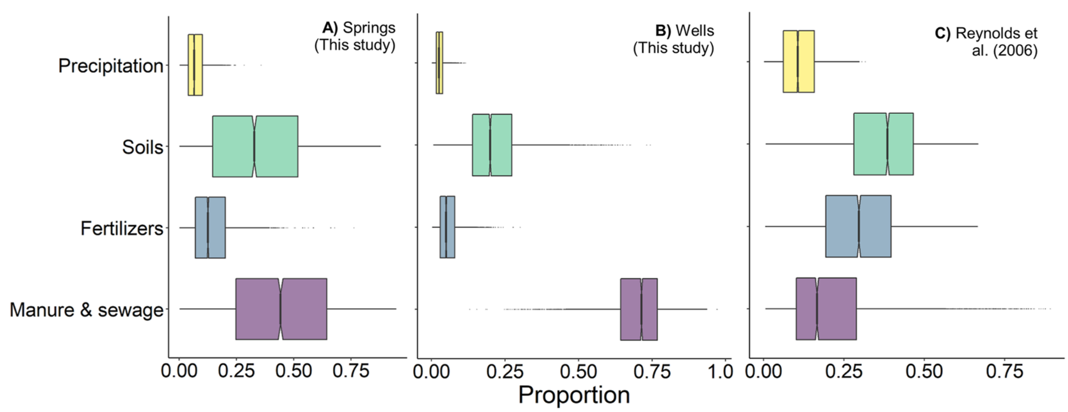

Figure 6. Bayesian endmember contribution box plots (%) for (a) springs (this study), (b) wells (this study), and (c) samples from Reynolds-Vargas et al. (2006) across the study area.

respectively. While precipitation nitrogen could be considered a minor source (<7.3%), fertilizer contributions related mainly to long-term coffee plantations can reach up to 14.4% ± 9.4% and 2.9% ± 1.7% in springs and wells, respectively (Figures 6a and 6b). Reynolds-Vargas et al. (2006) nitrogen source analysis offers a 30-yr old perspective of the nitrate legacy, with greater soils (36.4% ± 14.0%) and fertilizers (29.7% ± 13.6%) contributions and a significantly lower sewage/manure input (22.4% ± 17.9%). Figure S3 in Supporting Information S1 shows the $\delta^{15}N\text{-}NO_3^-$ spatial variability, where deep wells and high-elevation springs denoted depleted values (+1.9–7.7‰) and more enriched values in mid- and low-elevation wells and springs (up to +13.7‰). In addition, our data suggest no significant microbial denitrification occurs in the multi-aquifer system, since there is no evidence of $\delta^{15}N\text{-}NO_3^-$ or $\delta^{18}O\text{-}NO_3^-$enrichment coupled with a nitrate concentration decrease (Zhang et al., 2020). Potential nitrification (e.g., nitrification from ammonium fertilizers), which is inherent to shallow aquifers (Li et al., 2022) may occur within the Barva aquifer unit.

4.4. Land Use Change

Central Costa Rica is characterized by variable topography that includes mountain ranges, valleys, and plateaus. As a result, land use in this region is diverse and multifaceted and has been co-evolving with population growth during the last 40 years (Sanchez-Azofeifa, 2000). Coffee plantations have been the predominant crop in mid- to high elevations in the northern slope of this region. This agricultural activity has sustained a steady area (∼27%); however, rapid urbanization has changed coffee plantation distributions (Figures 7a and 7b). Livestock farming, particularly dairy farming, is also prevalent in the region. In this regard, pasture cover changed from 32.4% to 22.8% (Figure 7). While forest cover decreased from 29.5% (1979) to 13.4% across the study area (2019), a net increase of nearly 2% has been recorded in protected areas above 1,700 m asl to the expense of pastures (Figure 7b). These protected areas are either part of national parks or privately protected land under the PES scheme since the late 90s. The most abrupt land use change from 10.9% (1979) to 29.5% (2019) is related to urban growth (Figures 7a and 7b). In recent years, bare soils also increased (8.0%) due to land preparation for commercial, industrial, and residential developments. The latter has a direct impact on runoff generation and sediment loads to urban streams.

5. Discussion

5.1. Groundwater Isotopic Compositions and Recharge Mechanisms

Our water isotopes results call into question the commonly accepted hypothesis of vertical percolation between multi-aquifer formations as the main recharge mechanism. The isotopic difference between the Barva and Colima aquifers has been debated since the pioneering work conducted by the British Geological Survey (BGS, 1988). In this study, the authors identified similar depleted $\delta^{18}O$ compositions in the Barva formation and more enriched $\delta^{18}O$ values in the Colima formations (Figure 3 and Figure S1 in Supporting Information S1). While they found conflicting evidence of the isotope-altitude effect, they also noted that groundwaters become isotopically enriched with depth and assumed that the lower altitude contribution (mainly via urban recharge) was responsible for this unusual trend. Their rationale, however, only considered the effects of classical altitudinal distillation and secondary surface water evaporation as potential drivers of the isotopic variability. Later, Reynolds-Vargas et al. (2006) suggested that recharge to the shallow unconfined aquifer is primarily by direct infiltration, whereas recharge for the deeper semiconfined aquifer is either via percolation from the upper aquifer through pyroclastic beds or via infiltration from precipitation in the eastern part of the Central Valley (eastern topographic depression in Figure 1a). A recent study has demonstrated that the combination of high relief topography and rainfall type dynamics is translated into distinct isotopic spatial patterns within the BCS (Sánchez-Murillo et al., 2022). Basically, air masses traveling from the Caribbean Sea experienced a strong orographic effect, resulting in a notable depletion in rainfall isotope ratios across the central volcanic front, which in turn led to isotopically depleted signatures in groundwater and surface water within this high-altitude area and shallow responsive aquifers such as the unconfined Barva aquifer unit (Figure S1 in Supporting Information S1). In addition, isotope compositions within the unconfined aquifer unit exhibit uniform depleted compositions with distance, with no enrichment in the lower basin areas. If enriched vertical percolation in mid- and low elevations occurs, it should also affect the uppermost unconfined unit. Additionally, a topographic depression toward the eastern flank of the study area (Figure 1a) facilitates the recharge of Caribbean-type parental moisture (more enriched in $\delta^{18}O$), resulting in a clear enrichment within the deeper semi-confined units of the aquifer system. The latter is clearly depicted in the

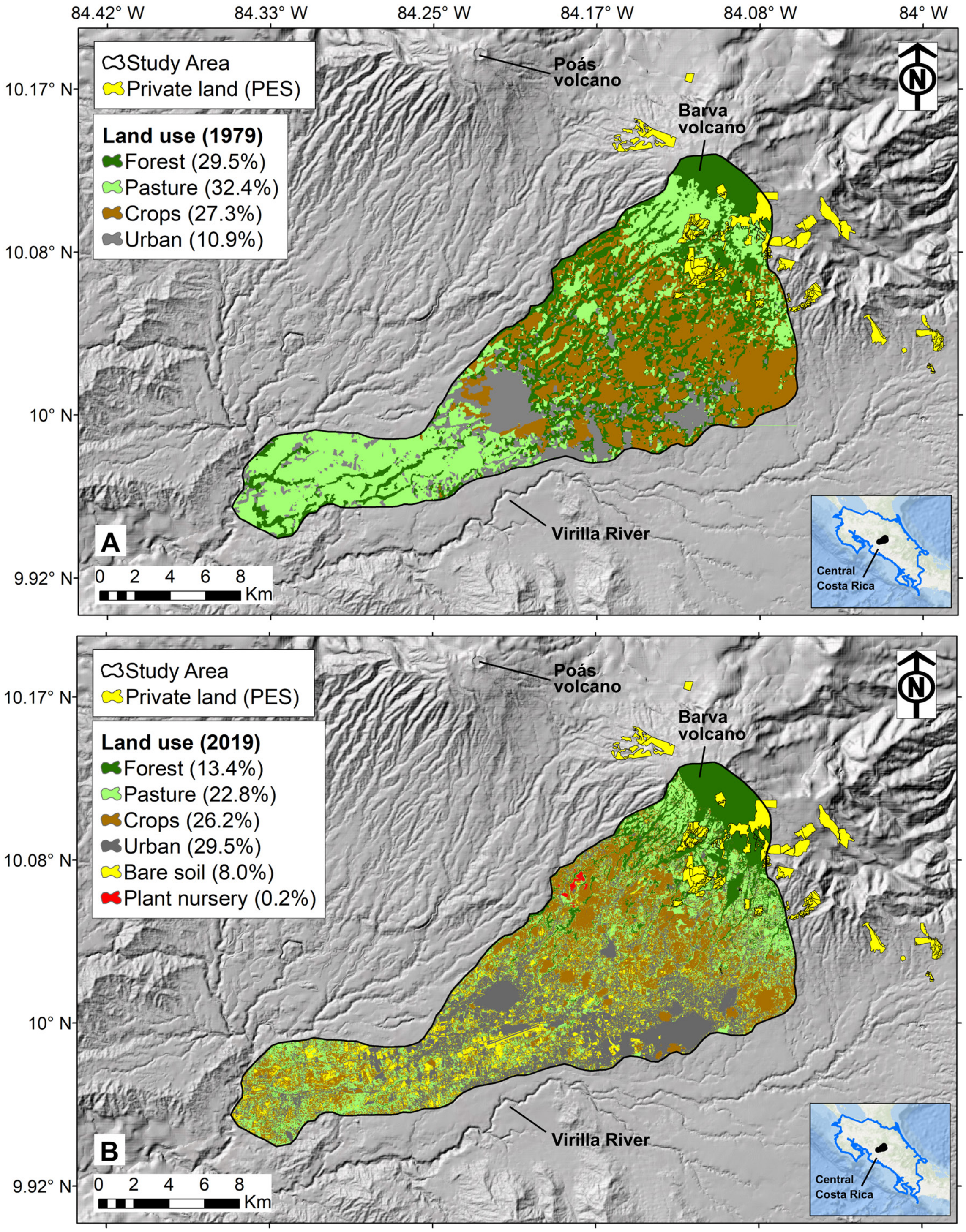

Figure 7. Satellite-based land use comparison between 1979 (a) and 2019 (b) across the study area. The black polygon denotes the best boundary limit of the Barva aquifer unit (Reynolds-Vargas & Fraile, 2009) and the yellow polygons denote private protected land under the national Payment for Environmental Services scheme (PES). The inset shows a regional overview of the study area in central Costa Rica.

isotopic and nitrogen separation across the BCS (Figure 3). Thus, vertical percolation from the unconfined unit toward the deeper formations cannot be the main recharge mechanism, since these formations exhibited $\delta^{18}O$ differences up to −4‰, with no evidence of significant thermalism or secondary evaporation. Low elevation contributions via highly polluted losing streams (Mena-Rivera et al., 2017) or through highly altered urban soils

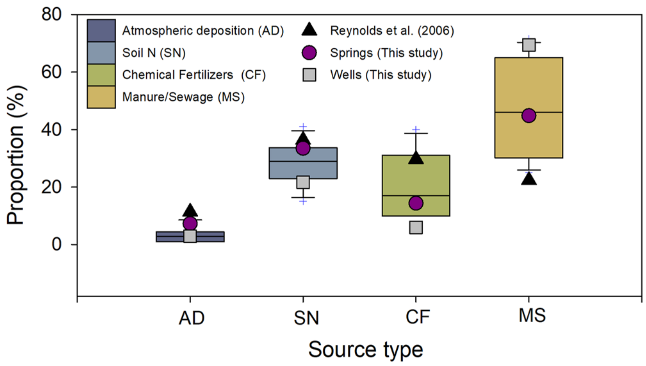

Figure 8. Box plot comparing groundwater nitrate contributions estimated by Bayesian isotope mixing models from this study and other tropical/subtropical studies (Fadhullahet al., 2020; Gribilla et al., 2020; Jung et al., 2023; Liu et al., 2021; Mao et al., 2023; Nyilitya et al., 2021; Reynolds-Vargas et al., 2006; Saka et al., 2023; Yu et al., 2020). AD: Atmospheric deposition; SN: soil nitrogen; CF: chemical fertilizers; and MS: manure and sewage.

could result in a clear deterioration of the groundwater quality over time. However, no other indications of groundwater quality issues (chemical or bacteriological) have been reported across this highly productive aquifer of central Costa Rica (Madrigal-Solís et al., 2022) during the last decades.

5.2. Groundwater Nitrate Legacy in a Highly Altered Tropical Urban Basin

The clear nitrate spatial variations across the BCS aquifer units (Figure 2) can be explained by the abrupt change in urbanization over the last 40 years. While urbanization has brought economic growth to the region, it has also put pressure on the environment and natural resources, particularly regarding water and air pollution, traffic congestion, and waste management. For example, urban growth has also impacted surface runoff, resulting in consistent urban flood events within the study area in recent years (Chen et al., 2021). More importantly, this urban center expansion has been characterized by mid- to high-elevation residential development (Figure 7a), where domestic septic tanks are still among the most common systems for storing sewage due to the lack of regionalized wastewater treatment. The latter is reflected in the nitrogen contribution increase from manure/sewage sources, changing from 22.4% (1990–2004, Reynolds-Vargas et al., 2006) to 69.4% in 2019 (this study).

In the case of the springs, high-elevation sites are mostly related to SN sources and low nitrate concentrations, whereas the low-elevation springs exhibited a closer relationship to septic nitrogen sources and greater nitrate concentrations (Figures 4 and 5). Some tropical basins are commonly characterized by high annual precipitation rates and high humidity conditions contributing to important natural organic matter mineralization fluxes (Elrys et al., 2021; Lodge et al., 1994; Pandey et al., 2009). In the BCS forested and protected headwaters, annual rainfall ranges from ~3,000 to ~5,000 mm between 2016 and 2022. In addition, as reported by Sánchez-Murillo et al. (2019), dynamic saturated areas within the Barva volcano edifice have a large capacity for solute leaching (e.g., DOC, nutrients) during high storm flows. This explains the predominant SN signature in high-elevation springs with nitrate values systematically below 5 mg/L (Figure 2). High-elevation spring systems were also governed by soil $\delta^{15}N$ compositions in a previous study (Reynolds-Vargas et al., 2006; Figure 5), while low-elevation wells denoted nitrogen isotope ratios near the CF and the manure/sewage domains.

Crop areas have steadily covered a quarter of the BSC area in the last four decades (Figures 7a and 7b), especially in mid-elevation regions (e.g., coffee plantations). However, crop areas have been re-distributed or diversified to favor residential development within mid- and high elevations. This is clearly depicted by the CF input change from 29.7% (1990–2004; Reynolds-Vargas et al., 2006) to 14.4% (springs) and only 6.0% in production wells, during the last 30 years. Overall, precipitation nitrogen inputs decreased during the last three decades, varying from 11.4% (1990–2004; Reynolds-Vargas et al., 2006) to 7.4% (springs) and 2.9% (wells) in 2019. While the overall forest cover across the basin has decreased from 29.48% to 13.39% with a significant loss between mid- and low-elevations, protected forested areas increased ~2% above ~1,700 m asl (main recharge area; Sánchez-Murillo et al., 2022) to the expense pasture areas (Figures 7a and 7b). The increasing forested area in the high-elevation sector is related to the establishment of the Braulio Carrillo National Park (1978; ~500 km^2; SINAC, 2023) and the advent of the Payment for Environmental Services (PES; Pagiola, 2008) in the late 90s. The most prominent recharge area within the BCS located above ~1,500 m asl includes over 1,000 private hectares under the PES scheme (Sánchez-Murillo et al., 2022) (Figure 1). In summary, 20 years ago, nitrogen major contributions to the groundwater system could be described as soils > fertilizers > sewage/manure > precipitation (Reynolds-Vargas et al., 2006), while recent and abrupt land use changes have also resulted in an isotopic and chemical nitrogen evolution toward sewage/manure > soils > fertilizers > precipitation.

5.3. Tropical and Subtropical Nitrate Groundwater Legacy

Figure 8 shows a comparison between this study and tropical/subtropical groundwater nitrate contributions, estimated by Bayesian isotope mixing models. In general, our results agree with pan-tropical/subtropical trends, where the major nitrogen median contributions in mixed land use scenarios are driven by manure and sewage (∼45%) > SN (∼30%) > CF (∼17%) > atmospheric deposition (AD) (∼3%) (Fadhullahet al., 2020; Gribilla et al., 2020; Jung et al., 2023; Liu et al., 2021; Mao et al., 2023; Nyilitya et al., 2021; Saka et al., 2023; Yu et al., 2020). However, our results suggest greater nitrogen AD (Villalobos-Forbes et al., 2021) and manure and sewage contributions compared to the tropics. Interestingly, nitrate groundwater legacy in the northern slope of the Central Valley of Costa Rica has evolved from ∼30% to ∼15% in chemical fertilizer contributions, and from ∼21% up to ∼69% in manure and sewage inputs during the last decades, as a direct result of the crop area conversion to meet the increasing demand in the residential areas. The identified nitrate groundwater legacy in the Central Valley of Costa Rica, evidenced by unprecedented decadal nitrate isotope data, could serve as a valid example of the potential impact of abrupt urbanization growth across the wet tropics.

6. Conclusions

The high levels of rainfall in the wet tropics can exacerbate the problem of groundwater nitrate pollution, as it can increase the rate at which nitrate leaches into the groundwater. This hinders nitrate pollution management in these areas, as the high levels of rainfall can lead to greater dilution of the pollutant in high-elevation saturated areas, making it harder to detect and manage. The combined isotopic and chemical data in this study enhance our modern understanding of legacy nitrogen sources in a complex groundwater system and their connections with land use change. Our findings also reveal a relevant process for tap water supply systems fed by a productive tropical and volcanic aquifer system, traditionally considered as pristine and with outstanding water quality. Our results confirm the early evidence of increasing groundwater nitrogen trends (Foster et al., 2002; Reynolds-Vargas et al., 2006), and they provide a new perspective on the potential nitrogen sources, which have remained enigmatic in past hydrogeological studies. Nitrogen and oxygen isotope values suggest a mixture of SN (most likely from forested recharge areas), sewage/manure, and in less degree fertilizers as a direct result of rapid population growth, urbanization, and unregulated land use management in the last 40 years in central Costa Rica. In this regard, it is important to point out that there is a lack of centralized wastewater treatment systems across the study area, where septic tanks are the most common solution (Durán-Sosa et al., 2022; Mena-Rivera et al., 2018) to store sewage waters for periods up to 5 years. Thus, the relatively high urban expansion (nearly +42.7% per decade) could be attributed as the main factor associated with the nitrate contamination processes in the BCS; however, other nitrogen sources from fertilizers, soils, and manure should be further investigated. Seasonal and spatial nitrate variations (concentration and sources) should also be addressed. Our data suggest incipient denitrification and potential nitrification (e.g., ammonium fertilizers) in the shallow unconfined aquifer unit. Our results highlight the urgent need for a multi-municipal plan to transition from domestic septic tanks to a regional sewage project and smart agricultural fertilization practices to effectively prevent future groundwater quality degradation. Overall, effective management of groundwater nitrate in the wet tropics requires a coordinated effort between government agencies, municipalities, farmers, and other stakeholders to ensure that groundwater resources are protected and managed in a sustainable manner. In addition, regular monitoring of groundwater quality can help to identify areas where nitrate pollution is a problem and determine the effectiveness of management strategies.

Global Research Collaboration

This study was conducted within a Research Coordination Agreement between the Universidad Nacional (UNA; Heredia, Costa Rica) and a public drinking water company known as Empresa de Servicios Públicos de Heredia (ESPH; Heredia, Costa Rica). Both institutions have been working together for almost a decade in the northern slope of the Central Valley of Costa Rica with the aim of improving the current understanding of precipitation deficits, groundwater recharge processes, and solute transport across a complex, tropical, volcanic, multi-aquifer system. This alliance has resulted in multiple international publications, local and international capacity building, and a continuous hydrometric and tracer monitoring network since 2014. Funding was obtained from three main sources: (a) Universidad Nacional (R-SM's previous academic appointment), (b) the International Atomic Energy Agency via research grants to R-SM and G-EH, and Empresa de Servicios Públicos de Heredia via research funds managed by L-CC. Sampling campaigns were coordinated between R-SM, R-SG, LD-RJ, and L-CC. Local researchers collaborated in the experimental design, sampling, data interpretation, and in writing the final manuscript. Results and interpretations are transferred in Spanish to the drinking water company staff and are used to improve their water resource management and planning.

Data Availability Statement

The data sets presented in this study are accessible at HydroShare, http://www.hydroshare.org/resource/a356a513daa34c58ba3c11bb20d2e3ea (Sánchez-Murillo, 2023) and as supplementary tables.

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