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Use of environmental isotopes to assess groundwater pollution caused by agricultural activities

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ABSTRACT

This work applied environmental isotope techniques to validate the results of previous studies on recharge sources in a rural area in central Chile (34.3° S and 71.3° W) and discern the origin of nitrate contamination in wells. Stream water and groundwater samples were taken during three surveys, two during spring snowmelt and one in low-water conditions. Chemical analyses included major cations and anions, isotope analyses included $^{18}\text{O}-\text{H}_2\text{O}$; $^2\text{H}-\text{H}_2\text{O}$; $^3\text{H}-\text{H}_2\text{O}$; $^{18}\text{O}-\text{NO}_3^-$ and $^{15}\text{N}-\text{NO}_3^-$. The stable isotope data show that surface water and deep groundwater present depleted isotope values associated with recharge from the Andes Mountains and that shallow groundwater has more enriched isotope values that reflect the contribution of local recharge from rainwater infiltration. Depleted isotope values observed in shallow groundwater show the effect of recirculated river water used for irrigation. These results are consistent with the conceptual groundwater model developed in previous studies. Some wells have nitrate concentrations above the allowable limit for drinking water. The stable nitrogen isotopes indicate that nitrate is associated mainly with urea and ammoniacal fertilizers, and nitrate is attenuated by denitrification. The results of this study are relevant to improving management of groundwater resources used for drinking water.

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1. Introduction

Worldwide, groundwater is the main source of drinking water for urban and rural populations due to its apparent ubiquity and reliability and because it is necessary only to drill a well near the area where water is requested [1]. However, groundwater systems are very complex and must be managed to guarantee sustainability, especially in terms of future water availability and quality [1–4].

In arid and semi-arid countries, groundwater is the main source of drinking water, if not the only one, as well as the source for uses such as irrigation or ecosystem protection; thus,

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conflicts between uses arise [1], mostly due to competition for water rights [5] and pollution resulting from agricultural chemicals [6] and wastewater [7]. Therefore, there is a consensus that groundwater management in agricultural areas must be improved [2–4].

It has been recognized for many years that nitrate is the main concern for groundwater quality in agricultural areas [8]. A widely published and discussed fact worldwide is that groundwater, especially in agricultural areas, is exposed to diffuse pollution, particularly nitrate from excess fertilization [8,9]. The impact of nitrate leaching on groundwater quality is a major concern around the world [10].

In Chile, groundwater is the source of drinking water for 53% of the urban population and 75% of the rural population [11]; therefore, the protection of aquifers is of paramount importance for people's wellbeing. While in Chile few studies on groundwater quality have been published, there are records of the effects of diffuse pollution on well water quality. In the Maipo River basin, high nitrate concentrations were detected in groundwater, the principal causes of which were irrigation with fecal water and disposal into the environment of urban and industrial waste without prior treatment, while fertilizer pollution was only a secondary source [12–14]. In a rural area of the Biobío Region, Claret et al. [15] analyzed chemical and biological contamination levels in groundwater, detecting high levels of total and fecal coliform contamination (93 and 100% of the samples, respectively) and nitrate levels above the drinking water standard (10 mg/l N-NO₃) in 14% of the analyzed cases. The understanding of groundwater pollution affecting rural drinking water wells is also important for the implementation of well head protection areas around the wells, which are not provided for in Chilean law [16].

The limited availability of information makes analysis of groundwater systems subject to significant levels of uncertainty. Previous studies in central Chile were based on the evaluation of hydrogeological data and the use of groundwater models to assess the water balance [17], estimating the groundwater recharge as a result that fits the aquifer water balance [18,19]. Uncertainty arises during the study of the agricultural impact on groundwater quality based on conventional nitrate modelling [14,15] because it is not possible to discern if the pollution sources are fecal contamination due to poor wastewater and livestock management or excess fertilization. Isotope techniques provide a complementary tool for the analysis of groundwater systems and to discern if the nitrate contamination sources are associated with fertilization or sewage [20–22].

Therefore, this study seeks to use environmental isotopes to improve our ability to study groundwater systems and discern whether nitrate contamination results from fertilization or infiltration of wastewater by applying isotope tools in a rural area of south-central Chile, specifically the lower Cachapoal River basin. This area was selected for two reasons: first, because it represents a typical irrigated valley where people get water from wells that are exposed to nitrate pollution, and second, because we have done previous studies in which the conceptual model of the groundwater system was defined [18,19].

2. Study site

The study area is located at 34.3° South; 71.3° West, about 100 km south of Santiago, Chile, in the O'Higgins Region (Figure 1(a,b)). The area is an agricultural valley that has an altitude ranging from 112 to 192 m.a.s.l, and an annual average precipitation of 650 mm/year. It is

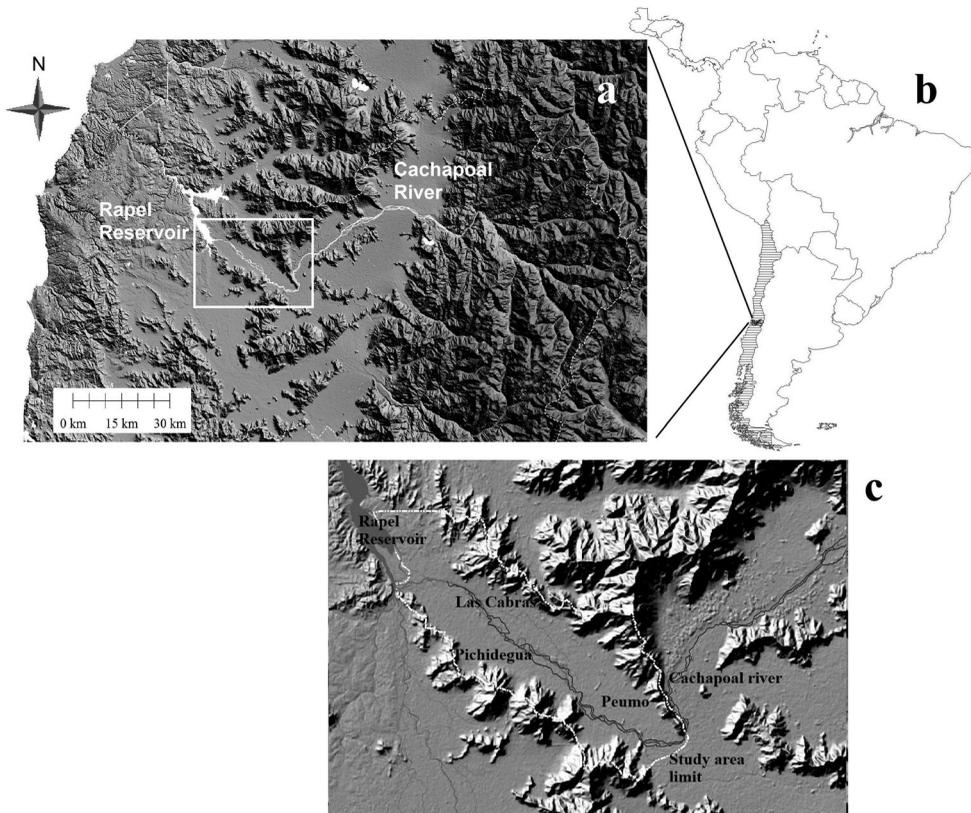


Figure 1. (a) Location of the study area and the Cachapoal River in the Libertador-General Bernardo O'Higgins Region; (b) Location of the above-mentioned region; (c) Image of the area (34.3° S, 71.3° W) showing the locations of the towns of Peumo, Las Cabras and Pichidegua and in white lines the borders of the study area.

bounded to the north and south by the Coastal Range. The upper border of the area is defined by the Cachapoal River, which bends around a section of the Coastal Mountains to enter a narrow 30-km valley. The area is bounded downstream by the Rapel Reservoir (695 M m^3), constructed in 1970. The headwaters of the Cachapoal River are in the Andes Mountains, and its watershed covers approximately 6500 km^2 . After crossing the Central Valley, the river bisects the Coastal Range, where the valley bottom forms the narrow southwest-to-northwest-oriented Peumo area. The river flow reaches a maximum in the austral winter when rainfall is greatest and during the spring snowmelt period.

There are three towns – Peumo, Las Cabras and Pichidegua – and several small villages in the area that get water from wells. These wells were drilled to provide drinking water (*agua potable rural*, APR) to rural communities.

The main economic activity in the study area is agriculture, predominantly intensive crop rotation west of the river and orchards and vineyards east of it. Agriculture requires irrigation from water that comes mostly from the river and to a lesser extent from groundwater wells within the valley. The irrigation canal network covers the entire valley and is composed of unlined earthen canals, most of which are more than 100 years old

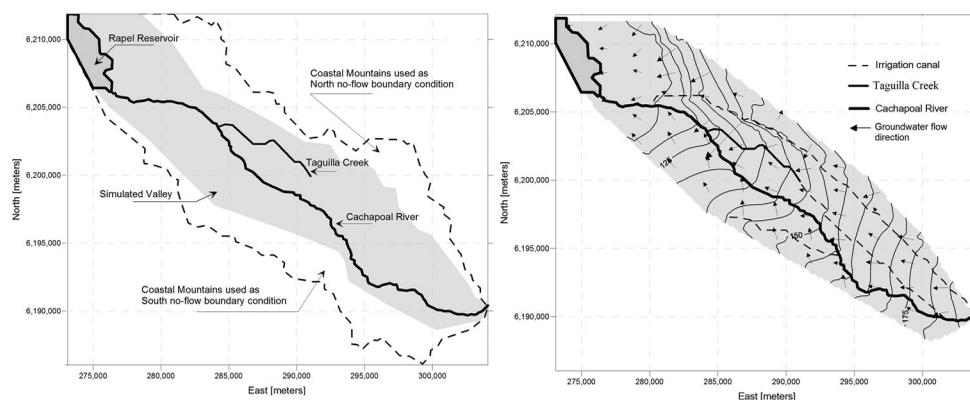


Figure 2. Left: a diagram of the groundwater system in the study area; right: Piezometric contours. Figure adapted from Arumi et al. [20].

(Figure 1(c)). The predominant soils in the valley are silty loams and silty clay loams in the agricultural areas and sandy gravel soil in the riverbed.

A conceptual model of the groundwater system developed in previous studies [18,19] identified a shallow unconfined aquifer composed of sand and gravel from fluvial deposits with an average thickness of about 75 m, formed along a 30-km valley boundary defined by the granitic Coastal Range (Figure 2), where the sediments have a saturated hydraulic conductivity ranging from 30 to 100 m/day [17].

Groundwater flows are strongly affected by the longitudinal gradient of the valley (0.3%). In the upper part of the valley, the groundwater system is recharged by the river, which behaves as a losing stream; however, at the end of the valley, the river receives seepage from groundwater, behaving as a gaining stream. Regional groundwater comes from mountain front recharge and rain infiltration in the Cachapoal watershed [17]. Local groundwater recharge is produced by precipitation during the rainy Chilean winter (May to September), accounting for the 25% of total annual recharge, while during the irrigation season (September to April), recharge is produced by seepage from the non-lined irrigation canal network (50% of total annual recharge) and percolation of excess irrigation (25% of total annual recharge) [18,23]. Figure 3 presents a diagram of these recharge dynamics.

3. Methodology

The methodology of this study was based on the use of stable isotopes as a tracer to complement previous work done in the study area. Although the study focused on groundwater quality, local recharge was also studied using surface water data. The sampling programme included three field campaigns: the first one took place in September 2016, during high-water conditions resulting from spring snowmelt and the prior Chilean irrigation season; 17 samples were taken.

The second campaign took place in April 2017, during low-water conditions (early fall and at the end of the Chilean irrigation season); 29 samples were taken, as more wells were included. Groundwater was collected from shallow and deep wells. The shallow wells were hand-dug and are used to extract water for domestic use or irrigation of small areas; they

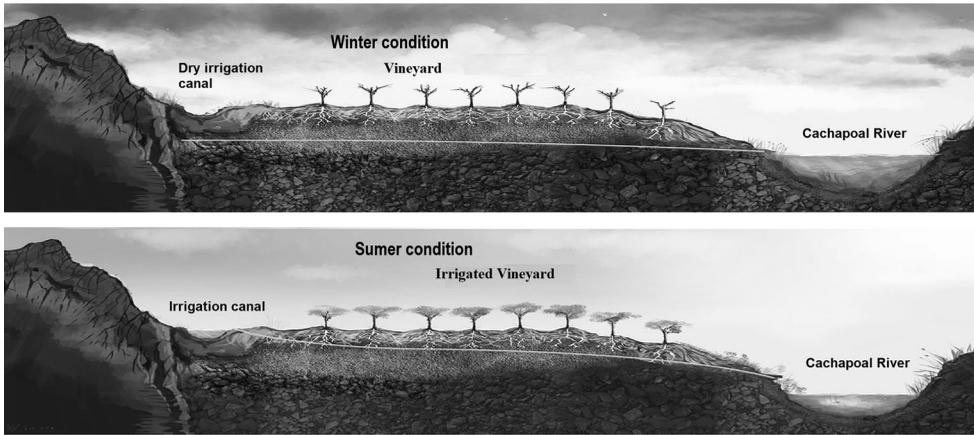


Figure 3. Conceptual model including a shallow water table located at a depth of 2.5 m during winter, with groundwater levels controlled by the river head, and the presence of a shallow water table located at a depth of 1.5–2.2 m during the irrigation season, during which the water table rises as a result of recharge from the unlined irrigation canals and irrigation losses. Figure adapted from Jara et al. [22].

have depths of less than 6 m, as the water table in the valley is located between 2 and 5 m below the surface. The deep wells were machine-drilled and have depths of 40–75 m; they are used for drinking water and irrigation of larger areas.

A third sampling campaign carried out in September 2017 focused only on sampling 7 additional deep wells (APR) that are water sources for rural communities. The well selection was based on the direction of the groundwater flow system and locations of local and regional recharge areas. Shallow and deep wells were selected along transects from the foothills to the river on both sides of the valley. The monitoring network included 19 shallow wells, 14 deep wells and 3 surface water stations along the river (Figure 4).

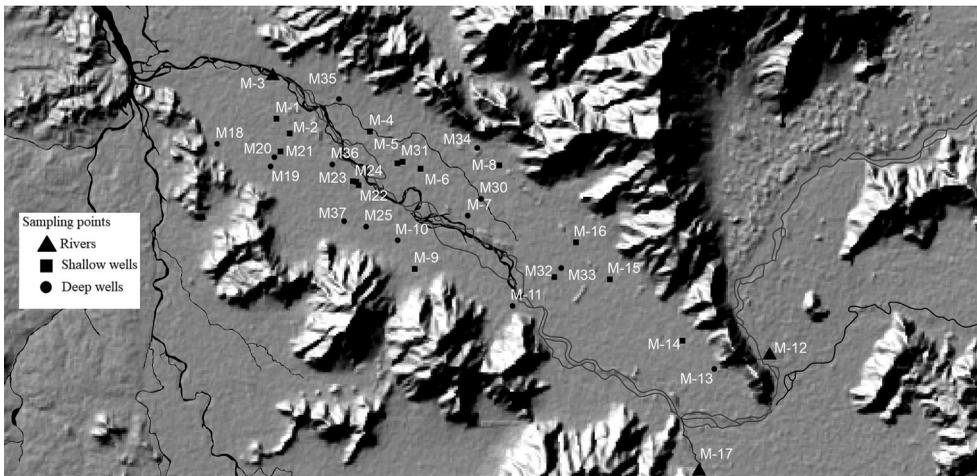


Figure 4. Location map of groundwater and surface water sampling network.

Groundwater and surface water were collected for chemical and isotope analyses. Wells were purged using their installed pumping systems for 15–30 min, depending on the time it took for the electrical conductivity value to become stable; temperature, pH, dissolved oxygen and total dissolved solids were also measured in the field. The samples were stored according to laboratory specifications. The chemical analyses included major cations and anions and the isotope analyses included $^{18}\text{O}\text{-H}_2\text{O}$; $^2\text{H}\text{-H}_2\text{O}$; $^{18}\text{O}\text{-NO}_3^-$ and $^{15}\text{N}\text{-NO}_3^-$. A subset of samples was selected for tritium analyses.

All the samples for isotope analysis from the two main sampling events were analyzed at the IAEA laboratory in Vienna using laser absorption spectroscopy for oxygen and deuterium and an elemental analyzer flash for nitrate isotopes and electrolytical enrichment/liquid scintillation counting for tritium. The analytical uncertainties were ± 0.1 and ± 1.0 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, and ± 0.4 ‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- . The analytical error for tritium measurement was ± 0.35 TU.

The samples from the third campaign were analyzed at the Environmental Isotope Laboratory at the University of Waterloo. The analytical uncertainties were ± 0.3 and ± 2.0 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively, and ± 0.5 ‰ for $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- . The analytical error for tritium measurement was ± 0.8 TU.

The chemical analyses were performed in a Chilean Nuclear Energy Commission (CCHEN) analytical laboratory in Santiago. Chemical analyses were performed on filtered ($0.45\ \mu\text{m}$) samples following the procedures established in Standard Methods, 20th edition [24]. Inductively coupled plasma optic emission spectrometry was used for Na^+ , K^+ , Ca^{2+} , Si^+ , Mg^{2+} ; high precision liquid chromatography (HPLC) for Cl^- , SO_4^{2-} , NO_3^- ; NO_2 and PO_4^{3-} ; and potentiometric titration for HCO_3^- . Detection limits in mg/l were: 0.1 for Cl^- , SO_4^{2-} and K^+ ; 0.25 for NO_3^- , NO_2 and PO_4^{3-} ; 1 for Na^+ , Ca^{2+} , Si^+ and Mg^{2+} ; and 20 for HCO_3^- .

4. Results and discussion

4.1. Chemistry data

All the results of the water chemistry and isotope analyses are presented as supplementary information in Table 1 (S1). The shallow and deep groundwater samples are characterized by a similar range of conductivity values: between 659 and 1014 $\mu\text{S}/\text{cm}$. Lower values are observed in surface water, ranging between 542 and 615 $\mu\text{S}/\text{cm}$. The shallow and deep groundwater is predominantly a Ca- SO_4 water type and in some groundwater HCO_3^- is predominant over sulphate (supplementary information S2). This is a common composition in watersheds of central Chile due to the lithology of Andean rocks and volcanic activity [11,17]. The shallow groundwater presents a wide range of nitrate concentration that varies between 0.1 and 82.8 mg/L reported as nitrate. The deep groundwater presents nitrate values between 1 and 70.2 mg/L. Surface water is characterized by low nitrate values in the range of 2 and 9 mg/L. Several groundwater samples present nitrate levels near or above the permissible limit of 45 mg/L in drinking water (Figure 5). Some of this groundwater is pumped from wells that are part of the APR network, which provides drinking water to rural communities. A plan view map (Figure 6) seems to show that higher nitrate concentrations in shallow and deep groundwater are observed in the western part of the study site, which could be related to the predominance of crop rotation and higher use of fertilizers in this part of the study area.

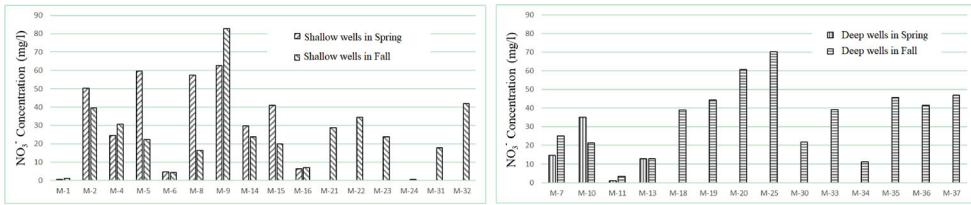


Figure 5. Distribution of nitrate concentrations in shallow and deep wells found in the September (Chilean Spring) 2016 and April (Chilean Fall) 2017 monitoring campaigns.

4.2. Environmental isotope data

4.2.1. $\delta^{18}\text{O}$ and $\delta^2\text{H}$

The data on stable isotopes in groundwater and surface water show a wide range of isotope compositions: between -9.7 and -12.9 ‰ for $\delta^{18}\text{O}$ and -69.7 and -93.9 ‰ for $\delta^2\text{H}$. The most depleted values are observed in the Cachapoal River, which is a reflection of the altitude of its headwaters, located in the high Andes (the highest mountain has an altitude of 5174 m), where precipitation has an annual average of 1200 mm/year. The most enriched isotope values, around -9.0 and -67 ‰ for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, reflect recharge by local precipitation [25]. The isotope data plotted along the local meteoric water line indicate that the water has not been affected by evaporation (Figure 7). In Figure 7 the deep groundwater isotope content is plotted between the depleted surface water values that reflect Andean recharge and the shallow wells that reflect local recharge. This pattern indicates that the deep aquifer is also receiving recharge from shallow groundwater in addition to regional recharge. The trend toward more depleted isotope values observed in the shallow groundwater is an indication of river water recharge via infiltration in irrigation channels and recirculation of river water in irrigated agriculture fields. A similar pattern of surface water recirculation influence in irrigated areas was documented in a nearby agriculture valley [19]. The influence of local recharge in the deep aquifer seems to explain the high nitrate content observed in some deep groundwater. The relationship between river water recirculation and high nitrate levels in the shallow aquifer is not so clear. The stable isotope data confirm the conceptual model presented in the study area section, which showed the influence of recirculated river water, which is a source of irrigation water, on the aquifer (Figure 7).

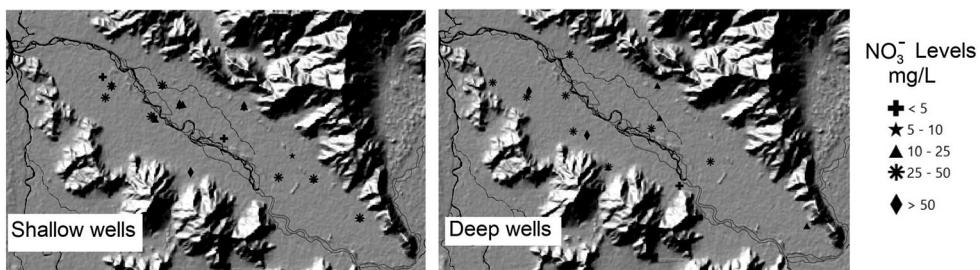


Figure 6. Plan view map that shows nitrate concentrations in shallow and deep groundwater in the study area.

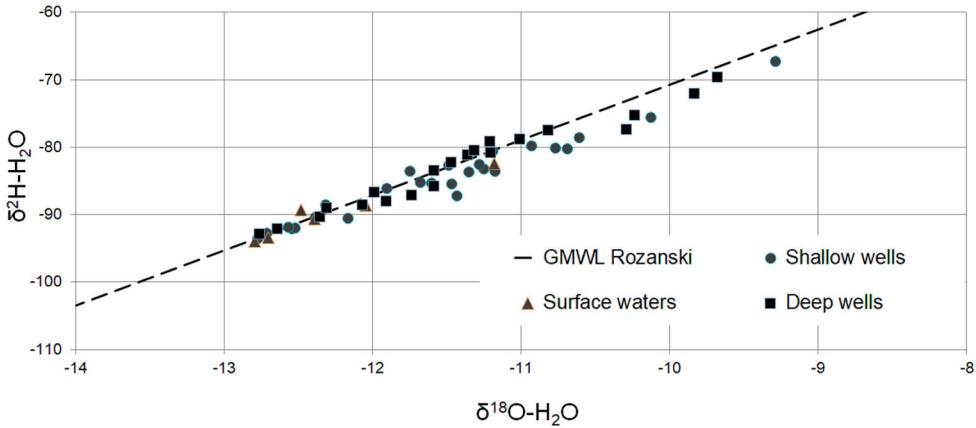


Figure 7. Data on stable isotopes in groundwater and surface water, plotted along the global meteoric water line.

4.2.2. Tritium data

The tritium data present values ranging from 1.6 to 2.1 TU in the Cachapoal River, 1.3 to 2.6 TU in shallow wells and 0.7 to 2.0 TU in deep wells; and there were two deep groundwater wells in which tritium was not detected. These results suggest that the shallow wells have a fraction of young water from rain recharge.

4.3.3. $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in nitrate

The isotope data presented a wide range of nitrate values, from +4.3 to +31.3 ‰ for $\delta^{15}\text{N}\text{-NO}_3$ and -2.4 to +16.3 ‰ for $\delta^{18}\text{O}\text{-NO}_3$. In the shallow groundwater samples, $\delta^{15}\text{N}$ values, should more closely represent the isotopic composition of the nitrate sources, ranged between +4 and 7.8 ‰; and the $\delta^{18}\text{O}$ values ranged between -2.4 and 2.5 ‰. This groundwater is characterized by nitrate concentrations ranging from 20 to 80 mg/L. A similar isotope range was observed in deep groundwater, which presented nitrate concentrations between 1 and 70 mg/L. The $\delta^{18}\text{O}$ values are in the range of values estimated using the model for nitrification of ammonium proposed by Anderson and Hopper [26], which assumes that 2/3 of the oxygen comes from water (-2.4 to +16.3 ‰ in this study) and 1/3 comes from atmospheric O_2 (+22 ‰). The isotope data could be explained by nitrification of urea and ammonium fertilizers affected by volatilization in the unsaturated zone. These are the most common fertilizers used in the study region [18]. The role of sewage from septic systems cannot be completely ruled out, although a similar range of Cl and Na in shallow and deep groundwater tends to discount this hypothesis.

A further analysis of the data on isotopes in nitrate regarding sources of nitrate and processes that affect nitrate in groundwater can be performed using Figure 8, which describes the isotope ranges of different sources of nitrate in groundwater. This figure shows a group of samples that are within the range of manure and sewage, although manure is not used in the study area and there is no hard evidence of contribution of nitrate from septic systems. It is well documented that volatilization of ammonia enriches the remaining ammonium in ^{15}N , which could explain the data observed at the study site [26]. There

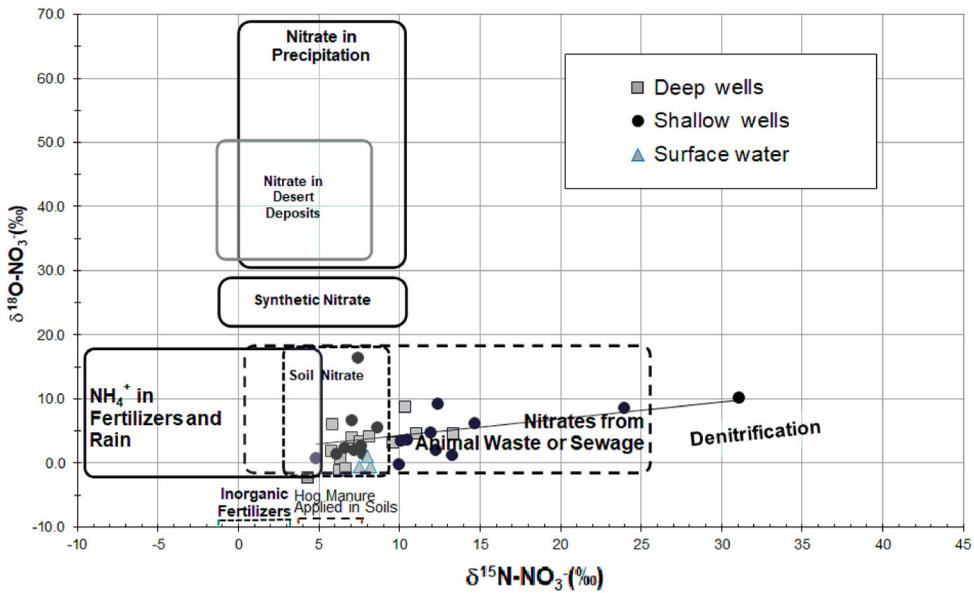


Figure 8. Data on stable isotopes in nitrate, surface water and groundwater.

are two samples that could indicate a trend toward more enriched $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, which is a typical trend for denitrification [27–29]. The most enriched isotope values, which present the greatest effects of denitrification, are observed in the shallow aquifer, a process which could be promoted by the presence of a high concentration of organic carbon and moderate winter temperatures; these findings are consistent with the lower nitrate values observed in some groundwater samples in central Chile [30].

5. Conclusions

The stable isotope data analysis results support the conceptual model of the groundwater system developed in previous studies. The role of regional and local aquifer recharge was illustrated by the stable isotope data. The role of recirculated river water used in the irrigated fields as a source of shallow and deep aquifer recharge was also demonstrated by the stable isotope data. This is an important issue for groundwater studies, as isotope analysis is an independent tool that supports groundwater modelling. Nitrate concentrations above the permissible level for drinking water were observed in the shallow and deep groundwater. The occurrence of high nitrate levels in the deep wells is a health concern because these wells are used to provide drinking water to rural communities.

The stable isotope data on nitrate suggest that the main sources of nitrate are urea and ammonium fertilizers and support previous evidence regarding the occurrence of denitrification as a process that attenuates nitrate in the aquifer. The pattern of high nitrate concentration observed in some APR wells, which provide drinking water to rural communities, should be considered by Chilean authorities with respect to the possible implementation of well head protection areas around APR wells in Chile as a public health protection measure.

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