

Application of Stable Isotope Analysis in Water Quality Studies

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ABSTRACT

Surface and groundwater contamination is a special concern worldwide due to its impact in drinking water and particularly in human health. In the north of Chile, water supply is a sensitive issue, due to the water resource scarcity (arid zone). In this region groundwater is the main component of water resources and due to its importance it requires a proper preservation of its quality, without compromising its use by the different users involved.

When groundwater has been contaminated, the most important aspects for assessing the causes and possible solutions are the identification of the polluters and the allocation of contaminant sources.

Stable isotopes are one of the most useful tools that have been used in studies of water resources in establishing causes of contamination (fingerprinting) and the sources that are affecting the water quality.

Stable isotopes have been used in several researches in Chile, highlighting its application in mining and agriculture settings. Industrial waters associated to mining projects have shown high sulfate concentrations while agricultural activities involve high nitrate loads to the groundwater system. In this sense, Isotope analysis generates relevant information determining the origin of contamination in the groundwater system.

The present paper is focused in the presentation of two applications of stable isotopes analysis. The first case is carried out in a Coastal Aquifer, to establishing the origin of sulfates in the groundwater system, and the second case, is carried out in an agricultural watershed to evaluate the presence of Nitrogen in groundwater, and its origin.

Keywords: Isotopes, Sulfates, Nitrate, Mining Projects, groundwater.

INTRODUCTION

Industrial activities such as mining or pork production, which correspond to the two study cases considered, are located in areas where other activities are developed in the land surface, which can also be contributing similar chemicals to the groundwater. Then, the problem is to distinguish the relative contribution of each potential source, in the resulting groundwater quality.

The following two study cases are presented:

- (a) Industrial activity associated to pork production in agricultural areas, where their manure are disposed as soil to supply nitrogen to the crops fields (potential source of Nitrates to the groundwater), and
- (b) Disposal of mining industrial water through irrigation of forested areas and the subsequent evapotranspiration (potential source of Sulfate to the groundwater).

The aim of the study is to evaluate dissolved ions presence and concentration levels (nitrates or sulfates, respectively) in groundwater (in selected pilot watershed) and to identify their origin from different potential sources. It is noted that conventional chemical characterization does not allow the identification of the sources that are contributing chemical elements to the groundwater.

Case A: agricultural area

In the selected pilot basin, there is intense agricultural activity. Both groundwater, pumped from deep wells recharged from local rains, and surface water, from a nearby river which comes from the mountains (it is originated from higher altitudes) are used for irrigation.

There is also an intense industrial activity associated with swine production, whose manures are disposed on crops areas located next to the pork production zones, in order to improve the soils quality.

The specific objectives of this study case are the following:

- To characterize the current nitrates concentration in groundwater, where intensive pork production industry is located.
- To identify and characterize the sources of groundwater nitrates in these areas.
- To identify and analyze the hydrogeological conditions involved in the nitrogen cycle and in the movement of nitrates.
- To identify fingerprints of the different sources of nitrates through the application of non-conventional techniques (water and nitrate isotopes).
- To monitor of those fingerprints in groundwater to assess relative contributions of each potential source. The monitoring was conducted for three years, considering seasonal measurements.

Case B: disposal of industrial waters over a coastal area by the irrigation of forested areas

Mining is located in the mountains, where the ore is mined and processed, being the copper concentrate the final product. The copper concentrate is driven from the Concentration Plant to the Port in the coast, where it is shipped to its final destination. The copper concentrate is driving by a pipeline using water for transport. On the coast, the copper concentrate is filtered and shipped, and the recovered water is disposed. There are various ways to dispose these industrial waters that

have been in contact with the copper concentrate and enriched in different chemical elements. However, the main chemical compound of concern in those waters is sulfate.

The main objective of this study is to assess the existence of a potential affection of the aquifer by infiltration of industrial water coming from the irrigation area. Despite the irrigation water is characterized by high sulfate concentrations, it is not possible to use only that mark, since in the study area there are other important sulfate sources, like marine waters (salt water intrusion or from the dissolution of the marine terrace which is part of the aquifer).

The specific objectives of this study case are the following:

- To characterize the current situation of sulfates in groundwater, specifically where the forested area, which is irrigated with industrial water, is located.
- To identify and characterize potential sulfate sources to the groundwater system.
- To identify and analyze the hydrogeological conditions involved in the sulfates cycle and its movement.
- To identify the fingerprint of the different sources of sulfates found in the study area through the application of non-conventional techniques (water and sulfate isotopes).
- To monitor those fingerprints in groundwater to assess the relative contribution of each potential source. The monitoring was conducted for seven years, considering an annual monitoring campaign.

METODOLOGY

A multivariate analysis was developed, including, among others, hydrogeological information, characterization of surface activities, and measurements of isotopic and chemical concentrations of surface waters and groundwater in these pilot basins.

Case A: agricultural area

Figure 1 presents the hydrogeological conceptualization of the pilot basin under study. Several measurements have been carried out in this area, in order to characterize the hydrogeology, hydrochemistry (major elements) and isotopes (water isotopes - $\delta^3\text{H}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$ - and nitrate isotopes - $\delta^{15}\text{N}$, $\delta^{18}\text{O}$ -). Over the three years of the project, six monitoring campaigns have been carried out, considering samples from 17 shallow wells, 12 deep wells and 5 surface water samples (see Figure 2).

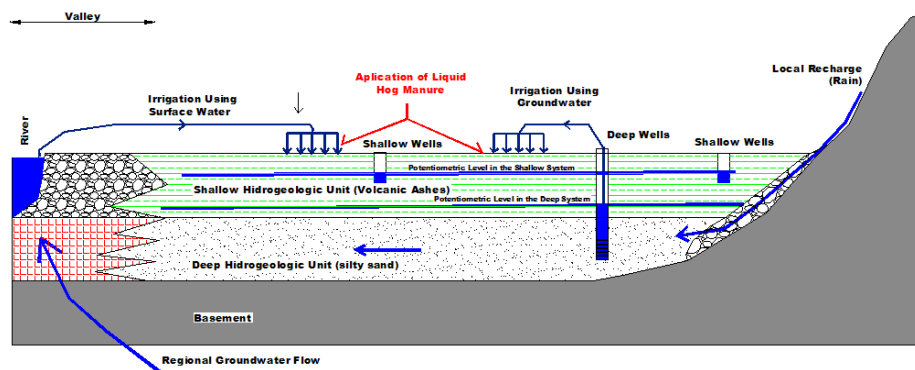


Figure 1 Hydrogeological conceptualization associated to the pilot basin where Nitrate is the main concern in the groundwater.

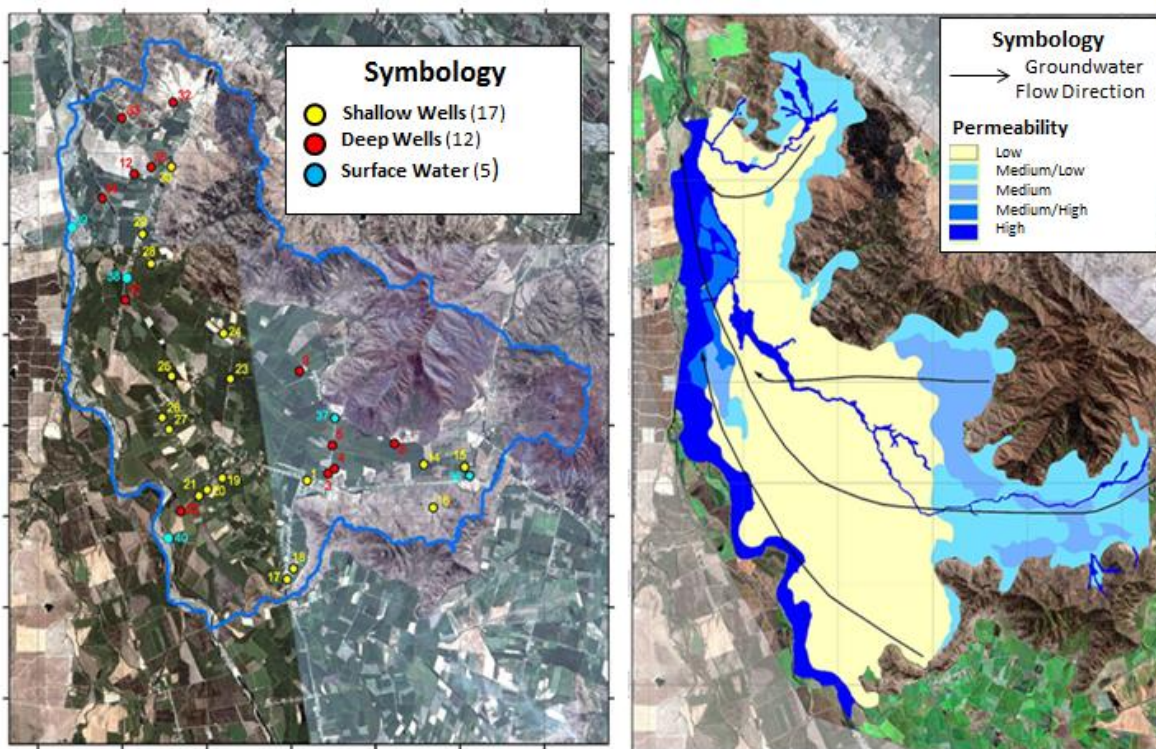


Figure 2 Sampling points and groundwater flow directions in the Pilot Basin where Nitrate is the main concern in the groundwater (agricultural area).

Case B: disposal of industrial waters over a coastal area by the irrigation of forested areas

In order to evaluate the different potential sources of sulfate observed in groundwater, it is necessary to characterize the ³⁴S isotope composition ($\delta^{34}\text{S-SO}_4$) for each potential source and evaluate its presence in the groundwater by the measurements in the monitoring wells existing in the area. Along with it, the isotopic water composition ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) has been characterized in irrigation waters, sea and groundwater in order to verify the altitude at which the aquifer recharge occurs due to the fact that it is known that industrial water used in irrigation comes from another basin located at a higher altitude with an isotopic signature noticeably different to the natural waters of the basin.

Figure 3 presents the hydrogeological conceptualization of the pilot study basin. In this area, several measurements have been carried out in order to characterize the hydrogeology, hydrochemistry (major elements), and isotopes (water isotopes - $\delta^3\text{H}$, $\delta^{18}\text{O}$, $\delta^2\text{H}$ - and sulfate isotopes - $\delta^{34}\text{S-SO}_4$ -). Over the seven years of the project annual campaigns have been carried out, considering samples from 14 deep wells and 2 surface water samples (see Figure 4).

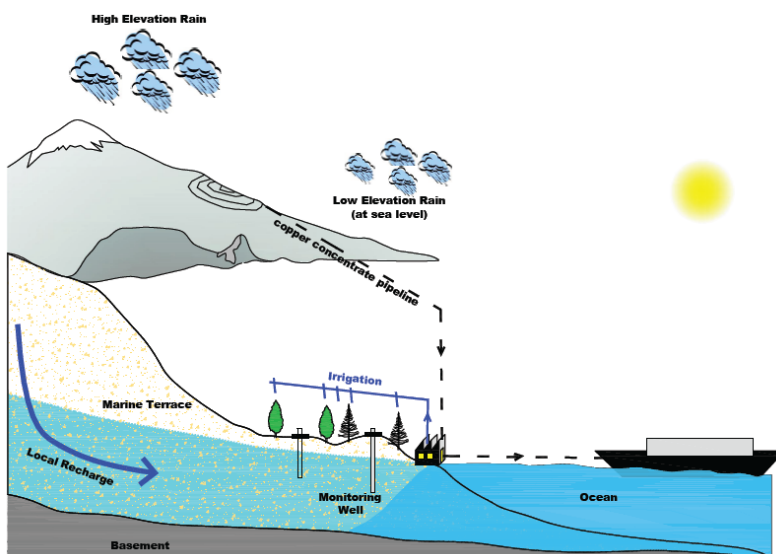


Figure 3 Hydrogeological conceptualization associated to the pilot basin where Sulfate is the main concern in the groundwater.



Figure 4 Sampling points and groundwater flow directions in the Pilot Basin where Sulfate is the main concern in the groundwater (coastal area).

RESULTS AND DISCUSSION

Case A: agricultural area

Nitrates in groundwater

Figure 5 presents the Nitrate measurements (mg N/l) in groundwater. Measurements show that, despite the intensive use of nitrogen sources in the ground surface, the measurements of N-Nitrate in groundwater show low concentrations, all close to 5 (mg-N / L), usually below 10 (mg-N / L).

In the aquifer system it is observed five shallow wells (from 16 monitored) with the higher nitrate concentrations. In these cases there is a nearby source which provides seasonally different nitrate concentrations, probably associated to irrigation

In the deep aquifer system low concentrations of N-Nitrates are observed. This situation it is explained by the presence of a superficial hydrogeological unit with low hydraulic permeability (ashes) which tends to isolate the deeper system from the surface. Then, the N-NO₃ is accumulated on or within these areas of slow water movement (located within the first three meters deep). Furthermore, due to the high clay content, with high nitrogen uptake capacity, probably as ammonium, it is prevented its transportation and transformation to nitrate. In the other hand, associated to the thickness of the clay layers and its low permeability, it is likely that nitrate it is been attenuated by the denitrification process (also seen by the isotopic measurements).

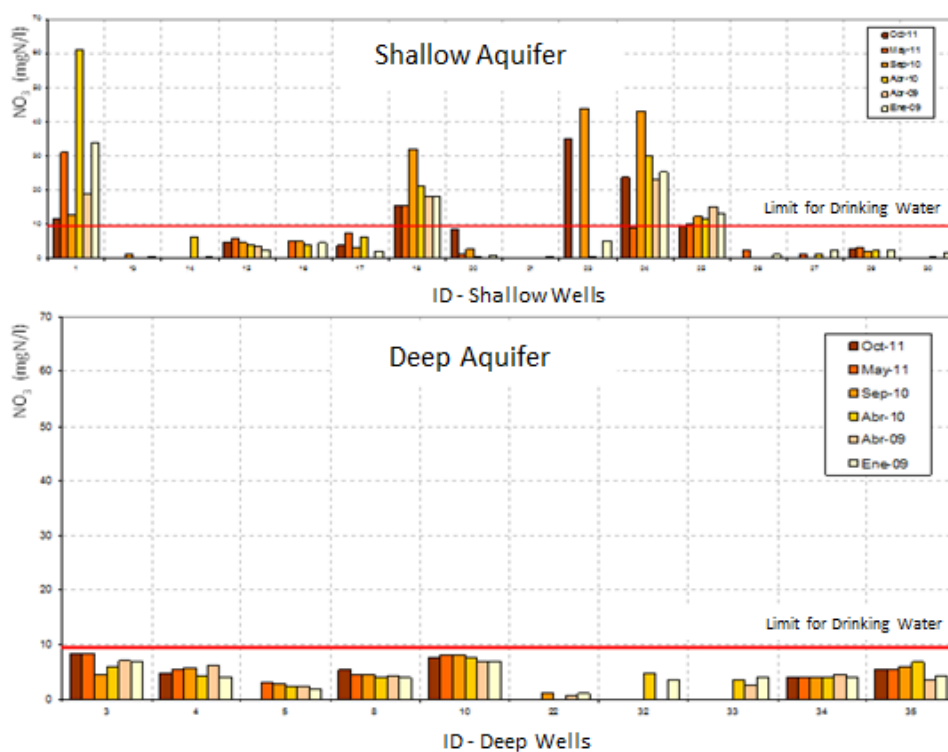


Figure 5 Nitrate Concentrations (mg-N/l) in groundwater in the pilot basin.

Origin of the Water

Measurements of stable water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$, see Figure 6) show that the origin of groundwater from the deep aquifer is different from the shallow system.

The waters of the deep aquifer are associated to local recharge (rainfall in the basin under study), presenting an isotopic signature more enriched. The recharge of the system is been produced by infiltration in foothill areas (see Figure 1).

The groundwater of the shallow aquifer (monitored in shallow wells) come from the percolation of irrigation excess and whose origin is the river crossing the area, which presents an isotopic signature more depleted in the stable isotopes of water (coming from higher altitudes).

Additionally some deep and shallow wells presents an intermediate isotopic signature corresponding to mixtures of local recharge and percolation of irrigation excesses.

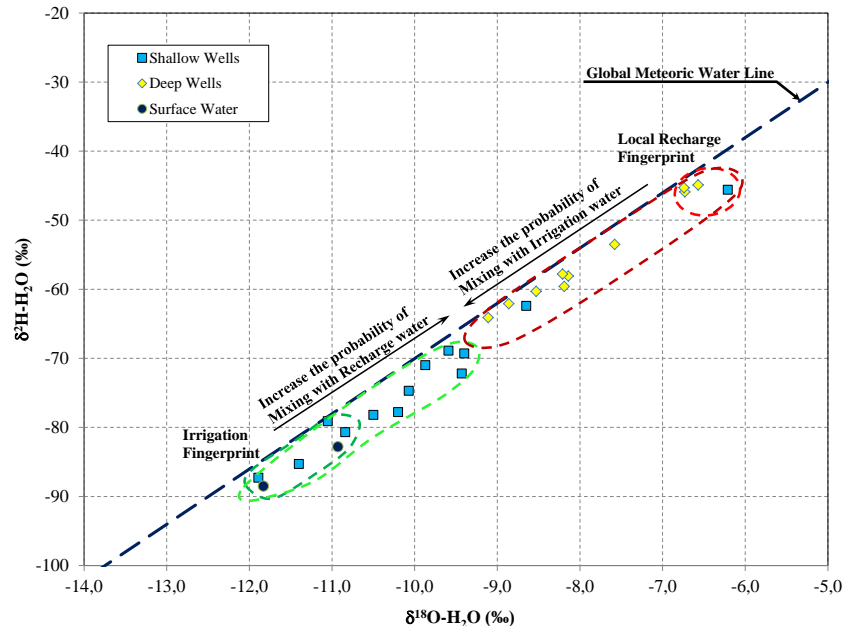


Figure 6 Oxygen-18 and Deuterium measurements in water samples.

Nitrate Origin

In the 5 shallow wells (groundwater from the shallow aquifer) with higher concentrations of nitrates, the isotopic signature of nitrate ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$) shows that the origin of nitrate corresponds to animal waste (see Figure 7), and it is being transported by water from the river (excess irrigation water). Urea volatilization is also observed (see Figure 8).

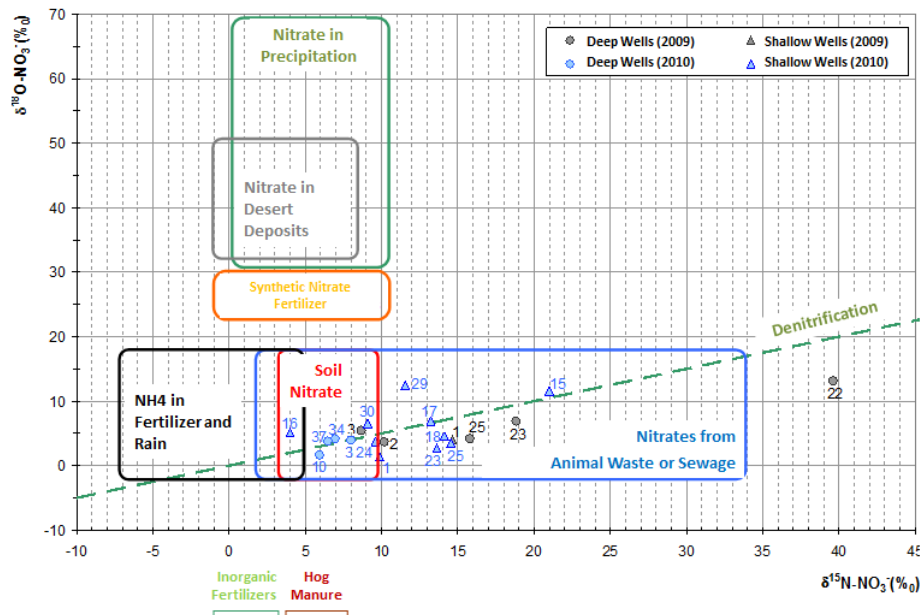


Figure 7 $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ measurements in water samples from shallow and deep wells.

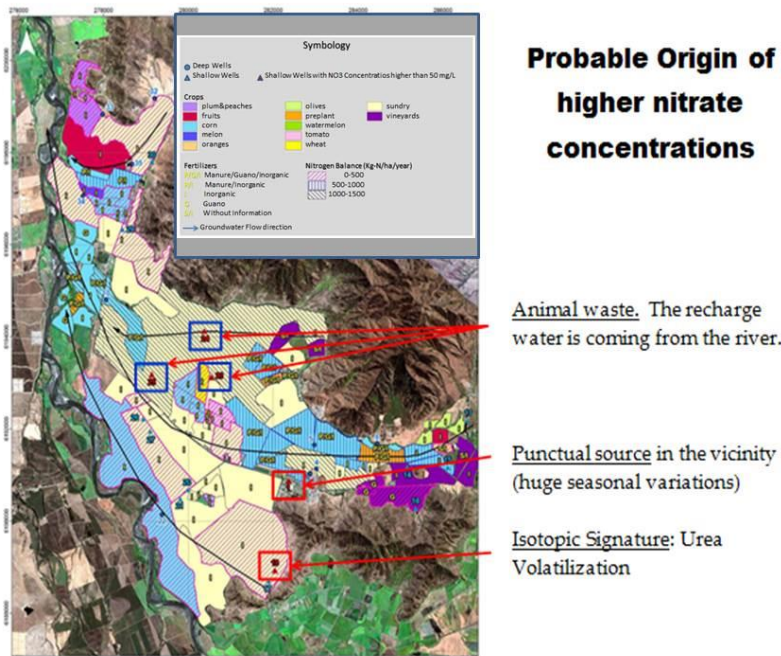


Figure 8 Probable Origin of higher nitrate concentrations in the shallow system.

Case B: disposal of industrial waters over a coastal area by the irrigation of forested areas

Sulfate in groundwater

Figure 9 presents the measurements of sulfate concentrations obtained in waters samples of the pilot area. The measurements are indicating that in addition to seawater, two wells present high sulfate concentrations (wells 5 and 8), which are located within the forested area which is being irrigated using industrial waters. The well 5 would be showing the groundwater quality in the exit area of the forestry field.

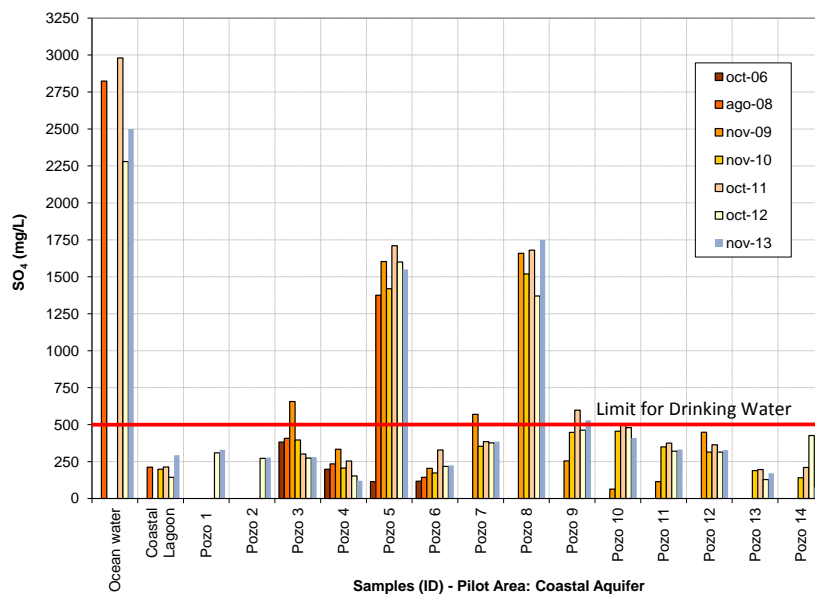


Figure 9 Sulfate Concentrations (mg/l) in water samples in the pilot basin.

Origin of the Water

Figure 10 presents the water isotopes composition of the different samples obtained in the study area ($\delta^{18}\text{O}$ and $\delta^2\text{H}$). From this figure, it is observed that industrial water used in irrigation presents an isotopic composition more depleted than groundwater and seawater, coinciding with its origin (high altitudes). Also, industrial water presents a significant degree of evaporation which shifts the typical isotopic signature (as highlighted with the red arrow). In the other hand, marine water presents a more enriched isotopic signature according to its origin in the hydrological cycle.

In the same figure it is showed that all groundwater are grouped (blue box) with an isotope composition showing a local recharge, presenting an isotopic composition very different from the irrigation water, so it was not observed a relationship between groundwater and industrial water. Similarly, the isotopic composition of groundwater also is not showing a relationship between groundwater and seawater.

Wells 5 and 8 presents an isotopic composition that is showing local recharge (see Figure 10), whose origin is different from the industrial water used in irrigation of the forested area.

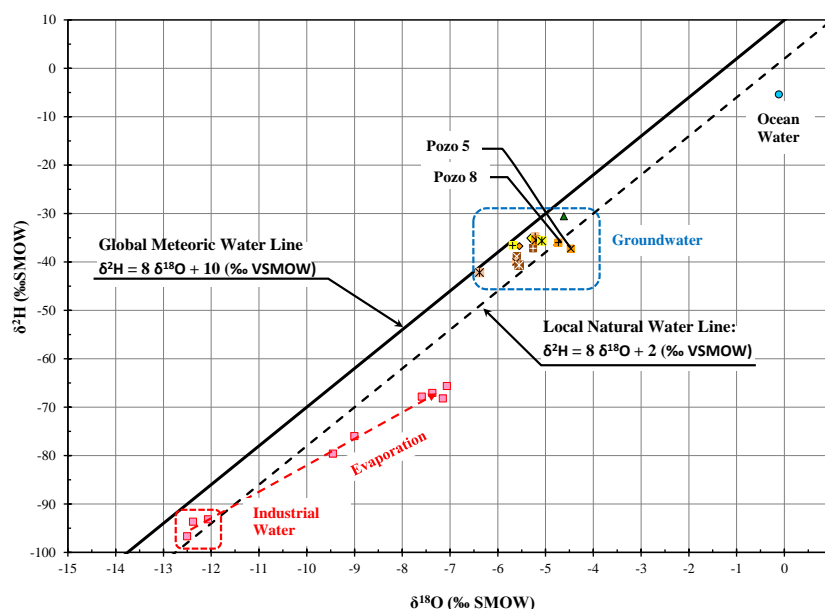


Figure 10 Oxygen-18 and Deuterium measurements in the different water samples (industrial and natural).

Sulfate Origin

Figure 11 presents the results of Sulfur-34 in Sulfate ($\delta^{34}\text{S-SO}_4$) along with sulfate concentrations measured at the different sampling points. In this figure it is observed that the industrial water used in irrigation have a very distinct $\delta^{34}\text{S-SO}_4$ isotopic signature with respect to those found in groundwater and marine water. Moreover, the sea water sampled during the different campaigns presents an $\delta^{34}\text{S-SO}_4$ isotopic signature located within the typical range of ocean water values (hatched in blue) which are very different to the industrial water signature.

In the other hand, groundwater are grouped significantly in an intermediate range of $\delta^{34}\text{S-SO}_4$ values (green box), with sulfate concentrations very low with respect to those characterizing the ocean and irrigation water. It is also possible to observe that there are wells whose waters have an isotopic signature within the typical marine range, which would reflect the contribution of marine sulfates to the groundwater system in these areas. The marine influence has two origins in the

study area; on the one hand, corresponds to saline intrusion caused by the exploitation of groundwater, and on the other, also responds to the dissolution of the salts contained in the unit associated to the marine terrace that is part of this aquifer. The second process has a natural origin but also presents an anthropogenic origin, where irrigation of the forested area plays an important role due to it proves waters with lower salts concentrations to the soil profile and to the unsaturated zone. To evaluate the process of contribution of marine sulfate it is analyzed the historical behavior of not only sulfate concentrations, but also of NaCl concentration and of the relative location with respect to the shoreline.

Particularly, in wells 5 and 8, it is observed (see Figure 11) that the source of sulfate in the groundwater corresponds to seawater (most likely correspond to the dissolution of marine sediments).

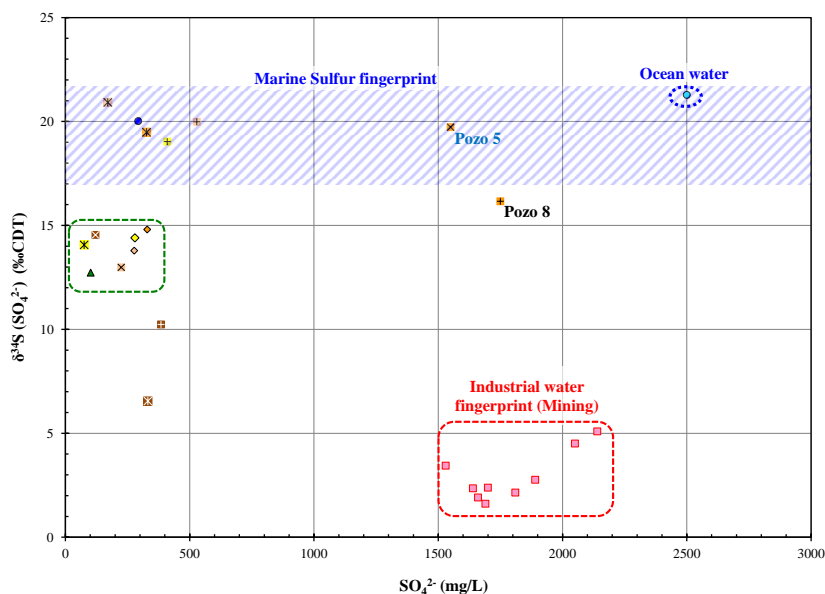


Figure 11 Relationship between $\delta^{34}\text{S}\text{-SO}_4$ measurements and sulfate concentrations.

CONCLUSION

The two study cases presented allow exemplify the application of isotope techniques in the study of the potential impact associated to a specific source of contamination to the groundwater system. Specifically, water isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$), Nitrate isotopes ($\delta^{15}\text{N}\text{-NO}_3$) and Sulfate isotopes ($\delta^{34}\text{S}\text{-SO}_4$), together with the hydrological, hydrogeological and hydrochemical analysis, give essential information in order to identify the origin of the contamination and the magnitude of the contribution associated to the different sources existing in a zone. This aspect is especially relevant when more than one potential source of a specific contaminant exist in the study area.

NOMENCLATURE

$\delta \text{ ‰}$ delta per mil, expression associated to the measures of stable isotopes, relative to an international standard, such as is noted in the following expression:

$$\delta_{\text{sample}} (\text{‰}) = 1000 \cdot [(\text{R}_{\text{sample}}\text{-R}_{\text{standard}})/(\text{R}_{\text{standard}})]$$

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