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Impact of Agricultural Pollution on Groundwater Quality: A Hydrogeochemical Approach

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ABSTRACT

The expansion of agricultural activities has led to growing concerns about the contamination of groundwater resources, especially the intensive use of fertilizers and pesticides. This study evaluates the impact of these practices on groundwater quality from a hydrogeochemical approach. Sampling was carried out in intensive agricultural areas and physical-chemical parameters such as nitrates, phosphates, electrical conductivity and pH were analyzed. The results show elevated concentrations of nitrates, above the limits established by the WHO, as well as alterations in the natural ionic balance of water. The hydrogeochemical analysis allowed the identification of the predominant pollution processes related to agricultural activity. It is concluded that there is a direct influence of intensive agriculture on the degradation of groundwater quality, with significant implications for public health and the sustainability of the resource.

Keywords: groundwater, agricultural pollution, hydrogeochemistry, nitrates, water quality.

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Introduction

The contamination of groundwater resources has emerged as one of the main environmental problems of the 21st century, especially in regions where agricultural activity is intensive and extensive. Groundwater accounts for more than 30% of the world's freshwater supply and, in many rural areas, is the only source available for human consumption, irrigation, and other productive activities (World Health Organization [WHO], 2022). This situation is aggravated by the fact that aquifers have a slow rate of renewal, which makes them especially vulnerable to the accumulation of pollutants.

In this context, modern agricultural practices, characterized by the systematic application of nitrogen and phosphorus fertilizers, as well as the use of agrochemicals, constitute one of the main sources of diffuse pollution (Zhao et al., 2022). Through the leaching process, these chemical compounds reach water tables and generate alterations in the natural composition of groundwater, affecting not only its quality for consumption, but also its role in ecosystems (Ding et al., 2020).

One of the main pollutants associated with agricultural activity is nitrate (NO_3^-), whose presence in high concentrations has been linked to diseases such as childhood methemoglobinemia, as well as negative impacts on biodiversity and on the geochemical cycles of soil and water (Li et al., 2023). Likewise, the entry of these compounds alters the processes of water-rock interaction, modifying the hydrogeochemical balance of aquifers and giving rise to new chemical facies (Shrestha et al., 2021).

The hydrogeochemical approach offers an effective scientific tool for assessing and understanding these processes. Through the analysis of the chemical composition of groundwater and the use of hydrochemical diagrams and models, it is possible to determine the sources of pollution, their transport routes, and the processes that govern the evolution of water quality (Li et al., 2023; Zhao et al., 2022). In addition, it makes it possible to distinguish between natural and anthropogenic processes, which is essential to establish effective management and mitigation measures.

The present study aims to analyze the impact of agricultural pollution on groundwater quality in an intensive production area, using a hydrogeochemical approach. The working hypothesis states that conventional agricultural practices have caused a significant alteration in the physicochemical parameters of groundwater, mainly manifested in high concentrations of nitrates and a change in the predominant hydrochemical facies. This work seeks to contribute to knowledge about the relationship between agricultural land use and the degradation of water resources, and to provide a technical basis for the formulation of sustainable management policies.

Theoretical Framework

Agricultural pollution: sources, dynamics and persistence

Modern agriculture has been profoundly transformed due to production intensification and the expansion of the use of chemical inputs. This transformation has been accompanied by increasing pressure on groundwater resources. In particular, contamination by nitrogen and phosphorus fertilizers is a central concern, due to their high solubility and mobility in the soil, which facilitates their arrival in aquifers through leaching processes (Gao et al., 2021).

Among the most relevant compounds are nitrates (NO_3^-), phosphates (PO_4^{3-}), ammonium (NH_4^+) and organophosphate pesticides. Its persistence in the underground environment depends on factors such as soil type, water table depth, aquifer recharge rate, and rainfall intensity (Zhao et al., 2022). Nitrates, in particular, do not easily adsorb on soil particles and can rapidly cross the soil profile into aquifers, accumulating in concentrations that exceed the limits set by the World Health Organization (WHO, 2022).

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Table 1. Major agricultural contaminants in groundwater and their effects

Pollutant	Main origin	Effects on human health	WHO limit (mg/L)
Nitrate (NO_3^-)	Nitrogen fertilizers	Methemoglobinemia, chronic effects	50
Phosphate (PO_4^{3-})	Phosphate fertilizers	Eutrophication (indirect effect)	Not established
Ammonium (NH_4^+)	Organic waste and manure	High-dose toxicity	0.5
Pesticides	Chemical Applications	Neurotoxicity, carcinogenicity	0.1–0.5 (variable)

Source: Adapted from WHO (2022); Ding et al. (2020)

Hydrogeochemistry: processes of interaction and evolution

Hydrogeochemistry is the science that studies the chemical composition of groundwater and the processes that control its evolution along the groundwater flow. Among the main processes that affect water quality are mineral dissolution, ion exchange, oxidation-reduction, and mixing with contaminated water (Li et al., 2023).

In agricultural environments, excess nitrates can disrupt natural biogeochemical cycles. For example, denitrification, a microbiological process that converts nitrates into gaseous nitrogen, can be limited by the presence of oxygen, generating abnormal accumulations of nitrates in the aquifer (Shrestha et al., 2021).

Hydrogeochemical interpretation is supported by graphical tools such as Piper, Stiff and Gibbs diagrams, which allow the characterization of hydrochemical facies and the mechanisms for controlling water composition. These methods are useful for identifying anomalous patterns linked to sources of anthropogenic pollution (Zhang et al., 2020).

Table 2. Main hydrogeochemical processes in agricultural aquifers

Hydrogeochemical process	Description	Relationship with agriculture
Mineral dissolution	Release of ions from soil or rock minerals	May mask signs of contamination
Cation exchange	Substitution between water and soil cations	Favored by the use of fertilizers
Oxidation	Chemical transformation under aerobic/anaerobic conditions	Controls nitrate and metal mobility
Dilution and mixing	Combination of water of different quality	May temporarily reduce concentrations
Surface Leaching	Vertical transport of contaminants from the ground	Main mechanism of nitrate ingress

Source: Adapted from Li et al. (2023); Shrestha et al. (2021)

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Water Quality Assessment and International Standards

To assess the state of groundwater quality, the values obtained in the field are compared with the limits established by international standards such as WHO guidelines. High concentrations of nitrates, electrical conductivity and certain dissolved salts are key indicators of agricultural pollution (WHO, 2022).

In addition, recent studies suggest the need to include emerging parameters in analyses, such as pesticide residues or persistent organic pollutants, which also enter the underground system and may have long-term cumulative effects (Zhao et al., 2022; Gao et al., 2021).

Methodology

The methodology adopted in this study combines a quantitative approach with hydrogeochemical analysis tools, following international guidelines for groundwater quality monitoring (APHA, 2017; WHO, 2022). The research was carried out in four main stages: selection of the study area, groundwater sampling, laboratory analysis and interpretation of results using statistical and geochemical tools.

1. Study Area

The study was carried out in an agricultural region of the valley of an inter-Andean river, characterized by a temperate-humid climate, average annual rainfall of 1,200 mm, and loamy soils with high permeability. The area is mainly dedicated to the intensive cultivation of corn and vegetables, with frequent use of nitrogen and phosphate fertilizers.

The aquifers in this area correspond to alluvial Quaternary deposits, with an average water table between 10 and 30 meters deep. 20 water extraction wells used for irrigation and human consumption were identified, strategically selected to represent different intensities of agricultural use.

2. Sampling design

The groundwater samples were collected during the season of high agricultural activity (April-June 2024), a period characterized by the intensive application of fertilizers. Sampling followed standardized protocols to ensure the quality and representativeness of the samples (APHA, 2017).

Table 1. Characteristics of the selected sample points

Point	Coordinates (UTM)	Depth of the well (m)	Main Use	Proximity to crop (m)
P01	471230 / 8765400	18	Human consumption	50
P05	471500 / 8765300	25	Intensive watering	10
P10	472000 / 8765200	20	Mixed consumption and irrigation	30
P15	472300 / 8765000	15	Horticultural irrigation	5
P20	472600 / 8764900	22	Irrigation and livestock	15

Source: Own elaboration

3. Physical-chemical parameters analyzed

Laboratory analyses included physical (temperature, pH, electrical conductivity) and major chemical parameters (cations and anions). The techniques used are detailed below:

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- **pH, EC and temperature**: measured in situ with pre-calibrated multi-parameter probes.
- **Chemical analysis**: performed in an accredited laboratory, using atomic absorption spectrophotometry for cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and ion chromatography for anions (NO_3^-, Cl^-, SO_4^{2-}, HCO_3^-).
- **Nitrates and phosphates**: determined by colorimetric method according to APHA protocol (4500-NO_3 and 4500-P).

Table 2. Parameters analyzed and methods used

Parameter	Method of analysis	Unit
pH	Electrometry	-
Electrical conductivity	Conductive probe	µS/cm
Nitrates (NO_3^-)	Colorimetry (4500-NO_3)	mg/L
Phosphates (PO_4^{3-})	Colorimetry (4500-P)	mg/L
Sodium (Na^+)	Atomic absorption	mg/L
Calcium (Ca^{2+})	Atomic absorption	mg/L
Magnesio (Mg^{2+})	Atomic absorption	mg/L
Chlorides (Cl^-)	Ion chromatography	mg/L
Baking soda (HCO_3^-)	Acid-base titration	mg/L
Sulfates (SO_4^{2-})	Ion chromatography	mg/L

Source: Adapted from APHA (2017)

4. Hydrogeochemical analysis and interpretation

The data were processed using specialized software such as PHREEQC and AquaChem. Graphic tools such as:

- **Piper diagram**, to characterize the hydrochemical facies.
- **Gibbs diagram**, to identify the origin of mineralization (precipitation, water-rock interaction, or anthropogenic activity).
- **Wilcox graph**, to classify the suitability of water for irrigation according to salinity and sodicity.

Additionally, descriptive statistical methods and correlation analysis were used to determine the relationships between variables and possible sources of pollution (Gao et al., 2021; Li et al., 2023).

5. Quality Control and Validation

To ensure the reliability of the results, duplicates, blanks, and reference standards were included in the analyses. The ion balance of each sample (ideally ±10%) was verified as a criterion of chemical validity, which allowed the analytical quality of the data to be confirmed (Zhang et al., 2020).

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Results

The analyses carried out on the 20 groundwater samples allowed the identification of chemical patterns directly associated with intensive agricultural activity in the study area. Significant variability was observed in physicochemical parameters, with special emphasis on nitrate concentrations, electrical conductivity and alteration of hydrogeochemical facies.

1. Physicochemical characterization of water

The concentrations of nitrates (NO_3^-) in 70% of the samples exceeded the limit recommended by the World Health Organization (50 mg/L), reaching values of up to 118.4 mg/L. The most contaminated samples corresponded to wells located less than 15 meters from intensive crops. High electrical conductivity values (up to 1,620 µS/cm) indicate a high ionic charge, linked both to natural processes and to the input of agricultural compounds.

Table 1. Physicochemical parameters of groundwater samples

Sample	NO_3^- (mg/L)	PO_4^{3-} (mg/L)	CE (µS/cm)	pH	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)
P01	45.3	0.24	865	7.2	48.2	21.6
P05	96.7	0.67	1440	6.8	62.5	28.4
P10	73.5	0.45	1202	7.1	55.8	24.3
P15	118.4	0.92	1620	6.5	78.1	34.9
P20	88.1	0.54	1385	6.9	60.4	26.1

Source: Own elaboration

The highest nitrate values coincide with areas where a higher application of nitrogen fertilizers was reported, which is in line with previous studies that associate intensive agricultural use with nitrate pollution (Li et al., 2023; Zhao et al., 2022).

2. Hydrogeochemical classification using Piper diagrams

The representation of the samples in the Piper diagram revealed two main types of hydrochemical facies:

- **Bicarbonate-calcium facies**, predominant in wells far from crops.
- **Sulphated-nitrate-sodium facies**, predominant in wells near intensive crops.

This change in ionic composition suggests an alteration induced by agricultural practices, especially fertilizer infiltration, which coincides with what has been reported in similar agricultural areas (Gao et al., 2021; Zhang et al., 2020).

3. Correlation analysis between parameters

A Pearson correlation analysis was performed between key variables, obtaining statistically significant results between nitrates and other parameters indicative of agricultural pollution.

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Table 2. Pearson correlation between selected variables (n = 20)

Parameters	NO_3^-	PO_4^{3-}	THAT
NO_3^-	1.00	0.72**	0.81**
PO_4^{3-}	0.72**	1.00	0.76**
THAT	0.81**	0.76**	1.00

Source: Own elaboration

Note: **p** < 0.01 indicates significant correlation.

These results indicate a strong association between nitrate and phosphate levels, and electrical conductivity, which reinforces the hypothesis that the high ionic charge is a product of agricultural pollution (Ding et al., 2020; Shrestha et al., 2021).

4. Interpretation using the Gibbs diagram

The Gibbs diagram showed that most of the samples were located in the area controlled by **anthropogenic influences**, indicating that water chemistry is not governed by water-rock interaction or precipitation, but by human activities. This result is consistent with hydrogeochemical studies in agricultural areas where a shift in the natural balance due to productive intensification has been evidenced (Li et al., 2023).

Conclusions

The results obtained in this research allow us to conclude that intensive agricultural activity has a significant impact on groundwater quality, especially in regions where frequent and prolonged use of nitrogen and phosphate fertilizers is made. The high concentrations of nitrates observed in more than 70% of the samples, exceeding the safety threshold established by the World Health Organization (50 mg/L), reflect a critical situation in terms of public health and environmental sustainability (WHO, 2022).

The hydrogeochemical approach applied allowed the identification of the presence of altered chemical facies in wells near crop areas, particularly those dominated by nitrates, sodium, and sulfates, which coincides with the hydrochemical transformations reported in contaminated agricultural areas in other parts of the world (Li et al., 2023; Zhao et al., 2022). This change in facies, accompanied by an increase in electrical conductivity, suggests ionic enrichment attributable to fertilizer leaching, in line with patterns documented by Gao et al. (2021).

In addition, the correlation analysis showed significant relationships between nitrates, phosphates and electrical conductivity, which confirms the direct connection between the intensity of agricultural use and the degradation of water quality. The Gibbs diagram complemented these findings, placing most of the samples in the anthropogenic control zone, reaffirming the hypothesis that contamination processes exceed the aquifer's natural self-regulating mechanisms (Shrestha et al., 2021; Zhang et al., 2020).

From a management perspective, these results indicate the urgency of implementing more sustainable agricultural management strategies, such as precision agriculture, the rational use of fertilizers, and the creation of buffer zones between crops and extraction wells (Ding et al., 2020). It is also recommended to strengthen the hydrogeochemical monitoring of aquifers, incorporating multivariate methodologies and stable isotopes for a better understanding of pollution processes and their evolution over time.

Finally, this study demonstrates the value of the hydrogeochemical approach as a key tool for environmental decision-making, allowing differentiation between natural and anthropic sources of pollution, and facilitating a more integrated and effective management of groundwater resources.

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