Role of agricultural land practices in the behaviour of nitrates in groundwater

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Key Points:

- Quantitative assessment of nitrate contamination in groundwater
- Agricultural practices indirectly influence nitrate contamination in aquifers
- Two major systems for nitrates may exist at aquifer depths above and below 150 m

Abstract

Nitrate contamination is a major issue in aquifers that are being exploited for drinking water. Exceeding regulatory levels of nitrates in drinking water can cause acute and chronic health problems. In agricultural areas, aquifers are vulnerable to nitrate contamination due to the excessive use of fertiliser. This research study investigated the potential impacts of anthropogenic nitrates on the giant Guarani Aquifer System (GAS) in Brazil, where nitrogen-based fertiliser use had doubled from 2005–2016. The study results indicated that there exists two different systems for the behavior of nitrates in groundwater, above and below a 150 m depth of the aquifer. For the aquifer depth above 150 m, Cl^- (positive influence) and F^- (negative influence) were found to significantly influence NO_3^- contamination ($p < 0.05$). However, statistically significant relationships between NO_3^- and other influential factors were not found for the aquifer depth below 150 m. Even though agricultural practices do not pose a direct impact on NO_3^- contamination of groundwater, it was evident that anthropogenic inputs of NO_3^- could elevate the concentrations in the aquifer depth reaching 150 m.

1 Introduction

Groundwater contamination is a major environmental problem worldwide (Mor et al., 2006; Stuart et al., 2014; Wang et al., 2007). In addition to natural sources such as weathering of rocks or soil, human activities are a primary contributor to groundwater contamination. The contaminants percolate through soil layers, degrading groundwater. This can ultimately cause serious health issues when people utilise the contaminated groundwater as a drinking water source (Chen et al., 2016; Majumdar & Gupta 2000). It has been reported that over two billion people worldwide rely on groundwater for their primary water uses such as drinking water, agriculture and food production (Famiglietti, 2014).

Among different contaminants, nitrate (NO_3^-) contamination is a critical concern in terms of groundwater pollution and related health impacts due to intensive land use practices and the application of N-based fertiliser in agricultural activities. According to the United Nations Food and Agricultural Organization (FAO), rice, maize and wheat utilise over 85% of N-based fertiliser (FAO, 2006), while global demand for N-based fertiliser has increased from 110 million tonnes to 117.1 million tonnes during the period of 2015-2019 (FAO, 2020). These statistics indicate that there is a growing trend in the application of N-based fertiliser for agricultural production. Even though nitrogen is an essential element for plant growth, the excess application of N-based fertiliser can negatively influence the denitrification capacity of soil, leading to the leaching of N in the form of nitrates into groundwater during the transformation of N within the soil (Almasri & Kaluarachchi, 2004; Follet & Delgado, 2002; Menció et al., 2016).

The transport and fate of nitrates in subsurface environments and their influence on groundwater quality have been widely studied (Joshua et al., 2013; Kaçaroğlu & Günay, 1997; Maila et al., 2004). Nitrate is considered to be a highly mobile contaminant in groundwater due to its anionic form and solubility characteristics (Canter, 2019). Thus, nitrates can migrate longer distances from the source region when favourable surface water infiltration is present. Additionally, aquifers that have highly permeable subsurface materials and shallow water tables are susceptible to nitrate contamination (Mahvi et al., 2005). Past studies have shown that aquifers found around agricultural lands were contaminated by nitrates, exceeding the drinking water standards of World Health Organization (WHO) (Burkart & Stoner, 2008; Korbel et al., 2013; McLay et al., 2001).

This study investigated the potential impact of agricultural practices on nitrate contamination in groundwater, while accounting for typical parameters that influence nitrates behaviour in groundwater. The study was based in the giant Guarani Aquifer System (GAS), Brazil, and the research outcomes are expected to contribute to prudent land use management strategies to protect critical groundwater resources in a region.

2 Materials and Methods

2.1 Study area

The study was carried out in a catchment located within the Paraná sedimentary basin, South Brazil (Figure 1). The hydro-stratigraphy of the Paraná basin consists of multi-aquifer systems, comprising sandstones and basaltic sediments (Campos, 2000). Groundwater primarily occurs within the interflow zones and along the basalts and diabases joints, where interbedded sediments increase the porosity of rocks. The GAS of Triassic-Jurassic age is the largest aquifer system within the Paraná sedimentary basin (extends over 1.2 million km^2 with an average thickness of 300-400 m), which mainly composes of silty and shaly sandstones of fluvial-lacustrine origin and variegated quartzitic sandstones (Araújo et al., 1999). A detailed description of the general features of the study area is provided in the Supporting Information. The dominant land use within the study area are agricultural lands, which are widely utilised for sugar cane, soybean and corn, flooded rice farming and pasture, and followed by urban uses.

2.2 Sample collection and laboratory testing

Groundwater samples were collected from 78 free-flowing and pumped tubular wells drilled into the GAS, considering its geological formation within the study area. Geo-coordinates of sampling locations and agricultural land use fraction as well the lithologies of sampling wells are provided in Tables S1 and S2 in the Supporting Information. The dominant land use within the study area are agricultural lands, which are widely utilised. The physical parameters of groundwater, including temperature (T), dissolved oxygen (DO), pH, and electrical conductivity (EC) were measured *in situ*. Samples collected were stored in polyethylene bottles (50 L), transported to the laboratory and kept under 4°C until further analyses were carried out. The hydrogeochemical parameters of groundwater, including nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), bicarbonate (HCO_3^-), dissolved sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) were analysed. A detailed description of the analytical methods used, quality control and quality assurance procedures adopted, and the data set generated are provided in Tables S3 and S4 in the Supporting Information.

2.3 Data analysis

The factors that potentially influence the NO_3^- contamination in groundwater were quantitatively assessed using Bayesian Networks (BNs) modelling. BNs develop probabilistic relationships among variables that define a process/system based on the prior knowledge or expert opinion (Bonotto et al., 2018, 2019; Uusitalo, 2007). The relationships between variables are represented by a directed acyclic diagram, and its *Markov Property* indicates that each variable depends only on its immediate parent variables. The model parameters are estimated in terms of conditional probabilities for discrete variables and in terms of conditional regression coefficients for continuous variables. Further details on BNs modelling can be found elsewhere (Jayarathne et al., 2019; Scutari, 2010, 2013; Wijesiri et al., 2018).

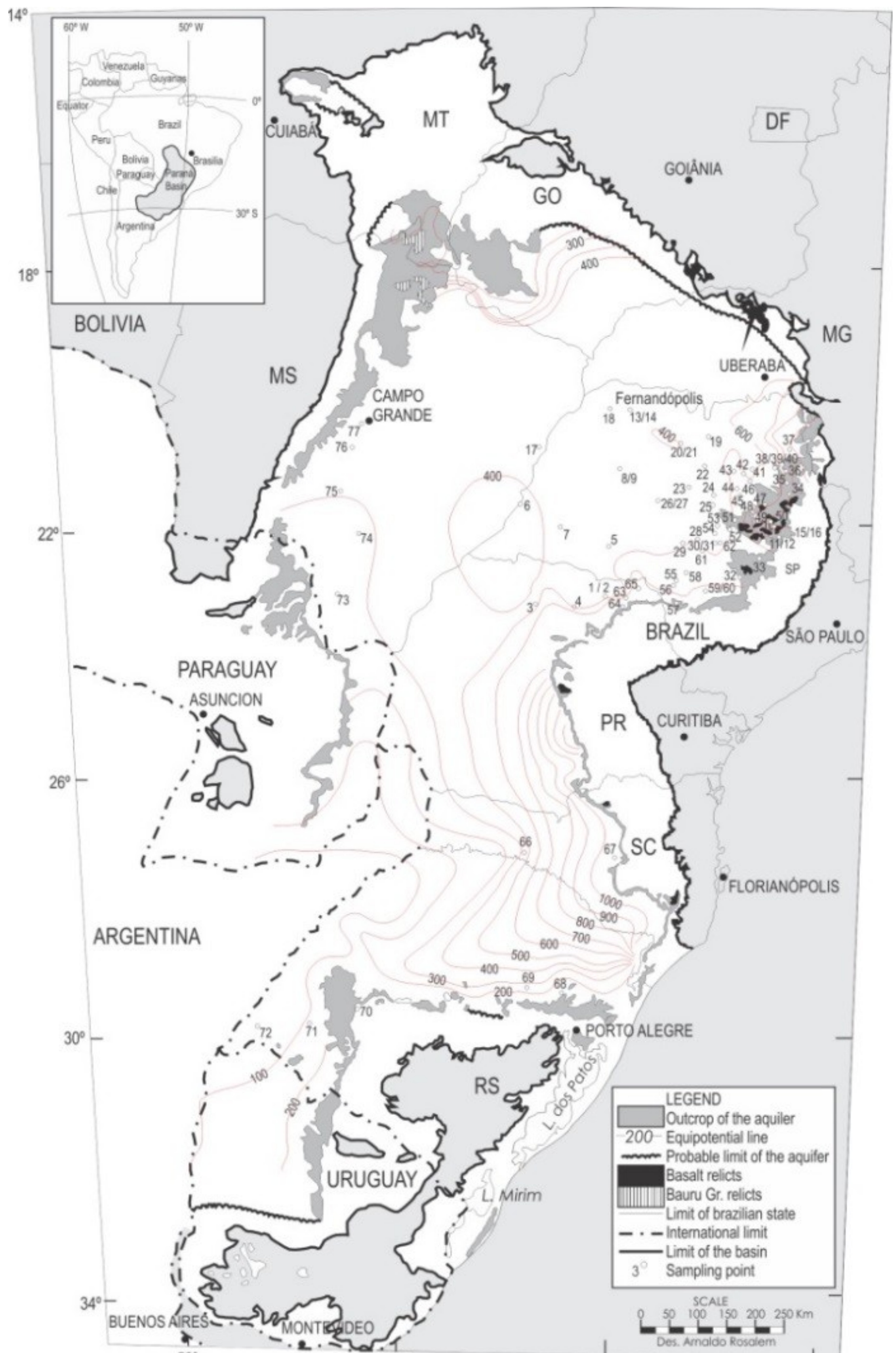

Figure 1. Sampling locations in the Guarani Aquifer System (GAS) within the Paraná Paraná sedimentary basin, South Brazil.

3 Results and Discussion

Once released to the surface soils, infiltration plays a key role in transporting nitrates to the aquifer. Figure 2 shows the variations in water table depth and nitrate concentrations at each well investigated in this study. The majority of wells indicate that lower the water table (situated in the close proximity to ground surface), the higher the nitrate concentration in groundwater. This pattern is more frequent in wells drilled up to a surface depth of 150 m (aquifer depth). This could be due to the larger number of wells above 150 m depth compared to the fewer number of wells below 150 m of surface depth. On the other hand, there can be two different hydrogeochemical systems of nitrates in groundwater above and below 150 m of surface depth. This was investigated using BNs modelling.

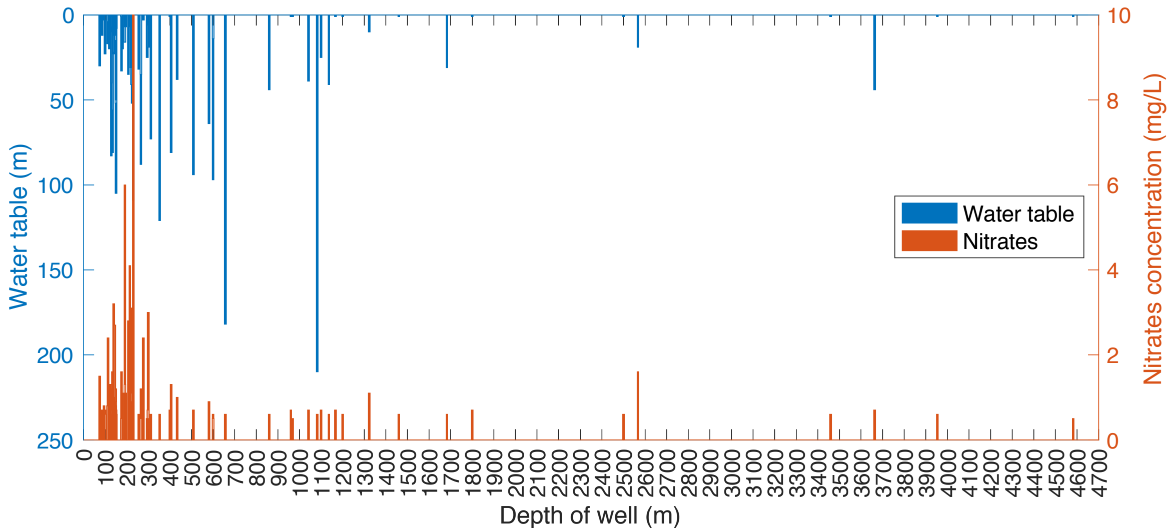

Figure 2. Variation in nitrate concentration in groundwater and water table against the depth of wells.

In the BNs analysis, those wells where the surrounding land use data was not available, were removed. Then, the remaining wells were separated, such that the aquifer depth is above 150 m and below 150 m. Further, the two data sets were screened by removing the samples where hydrogeochemical parameters were not available and by taking half the detection limit for the parameters that were measured below the detection limit. The outliers (those outside 1.5 times interquartile range) were also removed. The final data sets included 20 wells above 150 m depth and 37 wells below 150 m depth. However, it is important to note that those wells above 150 m ranged from 75–150 m, while the deeper wells ranged from 151–4,582 m. As such, the overall data set included 20 wells within the first 150 m of the aquifer, while there were 37 wells within 4.4 km.

The two data sets were then fitted with a simple BNs model shown in Figure 3. As such, the model considered direct interdependencies between nitrates concentration in groundwater and agricultural land use and 12 hydrogeochemical parameters (T, DO, pH, EC, SO_4^{2-}, Cl^-, F^-, HCO_3^-, Na, K, Ca and Mg) identified based on the research literature (see Figure 3 for relevant references). After performing leave-one-out cross validation (given the limited number of samples), F-test indicated that the overall model performance is satisfactory ($p < 0.05$) only for the wells reaching 150m depth. Further, model performance for aquifer depths reaching 150 m was also confirmed from the observed/predicted and residuals plots shown in Figure 4.

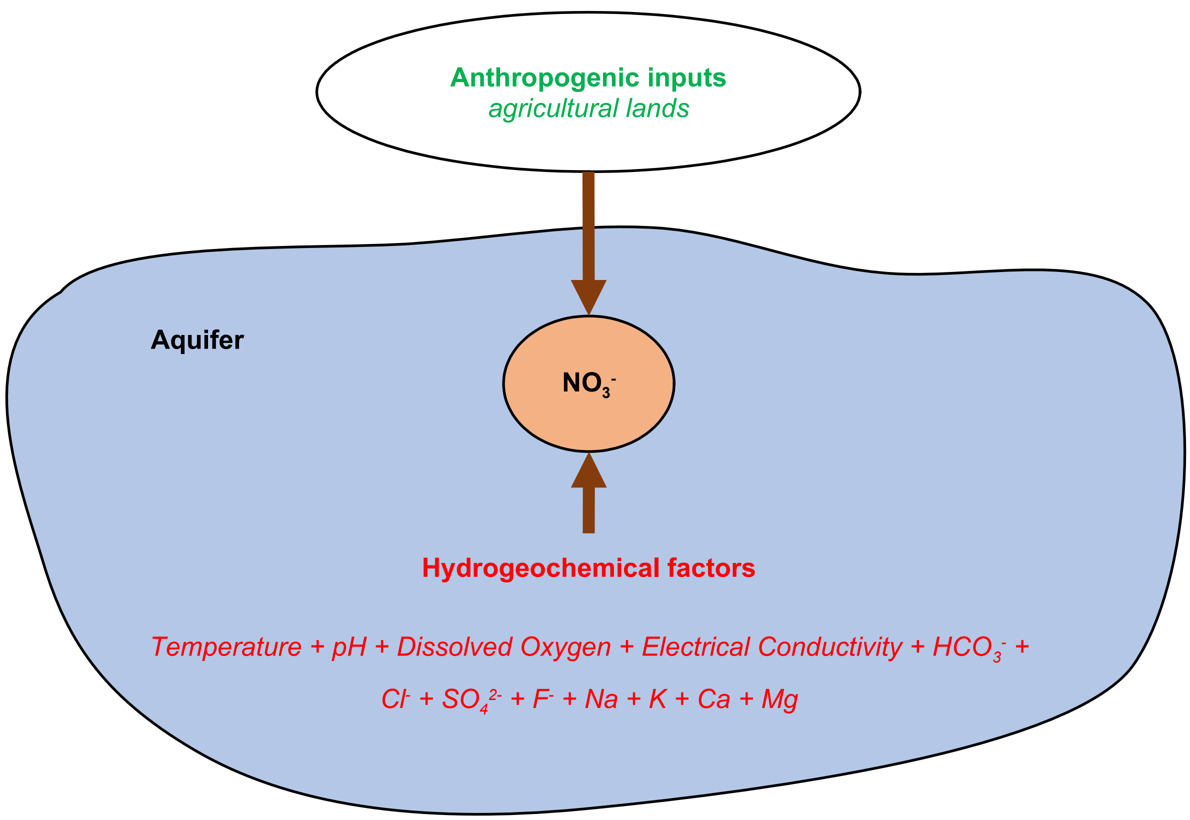

Figure 3. Bayesian Networks (BNs) model of the system of nitrates in groundwater. Note: interdependencies shown in BNs model were identified based on literature, such that NO_3^-/Temperature (Luk & Au-Yeung, 2002; Pfenning & McMahon, 1997); NO_3^-/pH (Menció et al., 2011; Yesilnacar et al., 2008); NO_3^-/Dissolved Oxygen (Rivett et al., 2008); NO_3^-/Electrical Conductivity (Menció et al., 2011); NO_3^-/HCO_3^- (Tang et al., 2012); NO_3^-/Cl^- and F^- (Menció et al., 2016); NO_3^-/SO_4^{2-} (Menció et al., 2016), NO_3^-/Na, K, Ca and Mg (Menció & Mas-Pla, 2008).

On the other hand, cross validation revealed that the overall model does not accurately replicate the behaviour of NO_3^- at depths beyond 150m (p – 0.329), implying that there is no statistically significant relationship between NO_3^- and influential factors. Additionally, to confirm the critical depth of 150 m at which nitrates might exhibit different behaviour, the model was fitted with data of wells above 200 m (26) and wells below 200 m (31). However, the overall model performance was not satisfactory for both cases (above 200 m: p – 0.183 and below 200m: p – 0.826 without statistically significant relationships between influential factors).

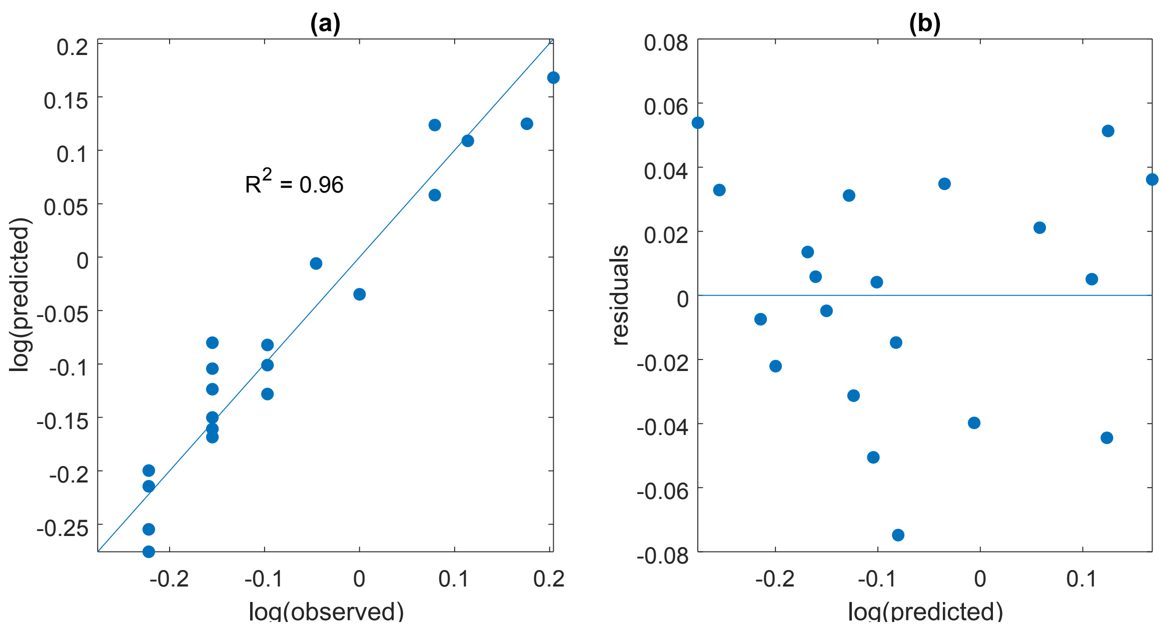

Figure 4. (a) Observed vs Predicted values plot; (b) Residual plot for aquifer depths above 150 m.

Table 1 shows the estimated conditional regression coefficients relating to nitrate behaviour within the aquifer depth above 150 m, which indicates statistically significant interdependencies between NO_3^- and Cl^- (positive influence) and F^- (negative influence). As the most influential factors, a 1% increase in Cl^- concentration in groundwater would likely increase the NO_3^- concentration by 0.099 mg/L, while a similar increase in F^- concentration would result in a decrease in the NO_3^- concentration by 0.17 mg/L. BNs modelling outcomes further indicate a positive influence of SO_4^{2-} on the prevalence of NO_3^- in groundwater. The prominent sources of NO_3^-, Cl^- and SO_4^{2-} ions in groundwater are mostly agricultural fertiliser, animal wastes and industrial and municipal sewage (Ako et al., 2014; Jalali, 2009). As such, the positive relationships between these ions can be attributed to fertiliser application in the study area.

Furthermore, the results show that lower NO_3^- concentrations could be observed in groundwater that is hot and basic (high temperature and pH), while cold and acidic conditions may increase the prevalence of NO_3^- (see negative relationships for temperature and pH in Table 1). It has been reported that during the nitrification of NO_2^- and NH_4^+ in the subsurface soil layers drained by groundwater, there is an increase in H^+ concentration in groundwater, indicating that reduced pH can increase NO_3^- concentration in groundwater (Menció et al., 2011; Stumm & Morgan, 1970).

As evident from Table 1, Na and Mg positively influence the prevalence of NO_3^-, whilst there is a negative influence from K and Ca. This implies that the increase in nitrates in groundwater is accompanied by the increase in Na and Mg in groundwater. Further, Table 1 shows that the increase in NO_3^- would likely decrease HCO_3^- concentration (negative influence), where there is high dissolution of carbonate rocks in the unsaturated zone (Baalousha, 2008). Such a relationship agrees with the findings by Kim et al. (2005). Based on the reaction stoichiometry for nitrification and oxidation of organic matter, Kim et al. (2005) noted that nitrate-generating processes produce an equivalent of nitrate by consuming the same equivalent of alkalinity, justifying the negative correlations between nitrate and alkalinity.

[a]Conditional density:
NO_3^- | AGR + T + pH + DO + EC + HCO_3^- + Cl^- + SO_4^{2-} + F^- + Na + K + Ca + Mg

Intercept (NO_3^-)	**AGR**	**T**	**pH**	**DO**	**EC**	**HCO_3^-**
0.00547	0.0616	-0.0553	-0.203	0.0820	0.0319	-0.158
Cl^-	**SO_4^{2-}**	**F^-**	**Na**	**K**	**Ca**	**Mg**
0.0989*	0.0507	-0.170*	0.136	-0.0505	-0.122	0.121

Leave-one-out cross validation
Significance code: * 0.05
Overall model p (F-test): 0.0402 (<0.05)

[a] Conditional density refers to the probability density function of a variable given each of its immediate parent variables
AGR – agricultural land area
T – water temperature
DO – dissolved oxygen
EC – electrical conductivity

Table 1. Estimated conditional regression coefficients for the proposed Bayesian Networks (BNs) model for aquifer depths above 150 m (Gaussian distribution, log-transformed data).

More importantly, the model indicates that a direct relationship between agricultural lands and NO_3^- is unlikely, meaning that there exist intermediate factors as the sources of NO_3^- to the aquifer. These could potentially include the mineral weathering through rock/soil-water interaction that generally exerts as an important control on groundwater chemistry, dominating the concentration of the major cations and anions. Silicates and carbonates are widely spread in the study area and their leaching affects the hydrochemical composition of the GAS groundwaters because of their reactivity and abundance in the magmatic and sedimentary rocks of the Paraná basin. However, given that the overall model performs satisfactorily, the estimated conditional regression coefficients indicate that 1% increase in agricultural land uses could elevate NO_3^- concentration by 0.062 mg/L. The influence of agricultural lands, in terms of fertiliser applications alone on NO_3^- concentration in groundwater might be low, but it is important to note that agricultural practices create a favourable environment for the prevalence of NO_3^-, which can be a challenging issue into the future. This is because of the increasing extent of Brazil's agricultural lands (as a fraction of total area: 31% in 1995, 33% in 2005 and 34% in 2016) (FAO, 2018), together with increasing urbanisation could change the hydrogeochemical environment in the aquifers.

4 Conclusions

Based on the giant Guarani Aquifer System (GAS) in Brazil, this study investigated the impact of agricultural land use practices on the nitrate contamination of groundwater, while accounting for the aquifer geochemistry. The results derived indicate that there can be two different hydrogeochemical systems of nitrates above and below the aquifer depth of 150 m. For the aquifer depth above 150 m, significant interdependencies were found between NO_3^- and Cl^- (positive) and NO_3^- and F- (negative). A 1% increase in Cl^- concentration in groundwater was found to elevate the NO_3^- concentration by 0.099 mg/L, while a similar increase in F^- concentration would decrease NO_3^- concentration by 0.17 mg/L. Importantly, it was evident that the agricultural land use fraction is unlikely to pose a direct impact on NO_3^- in groundwater, but indicated that there exists intermediate factors such as physicochemical properties of subsurface rocks/soils that potentially influence the transport of NO_3^- released from agricultural lands. However, the study found evidence of the influence of agricultural land use practices on NO_3^-.

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data is guided by the Queensland State Archive University Sector Retention and Disposal Schedule for research data, as well as other relevant legislation.

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