Environmental Earth Sciences (2018) 77:229
https://doi.org/10.1007/s12665-018-7395-5

ORIGINAL ARTICLE

Nitrogen and oxygen isotopes as indicators of pollution sources in the Faxinal Dam watershed, Southern Brazil

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Received: 9 May 2017 / Accepted: 28 February 2018 / Published online: 15 March 2018

Abstract

Isotopic signatures of δD-H_2O, $\delta^{18}O$-H_2O, $\delta^{15}N$-NO_3^-, $\delta^{18}O$-NO_3^- and $\delta^{15}N_{Fertilizer}$ isotopes were used in order to evaluate the impact of agricultural inputs (fertilizers and calcium nitrate) and sewage effluents on the water of tributaries of the Faxinal Dam, which supply the city of Caxias do Sul in Southern Brazil. δ^2H and $\delta^{18}O$ were identified by spectroscopy laser absorption tunable diode-type cavity ring-down spectroscopy, while the isotopic ratios of ^{15}N and ^{18}O in nitrate were determined by isotopic ratio mass spectrometry, applying the chemical denitrification method. The results showed that most of the analyzed samples are compatible with the Global Meteoric Water Line, Local Meteoric Water Line and Carlos Barbosa Wells and Fountains Tendency Line, except for the Fx-07 sample that presented greater similarity to $\delta^{18}O$ values for groundwater. The isotopic signatures of $\delta^{15}N$-NO_3^- versus $\delta^{18}O$-NO_3^-, in the great majority of the samples, pointed out the influence and the contribution of the fertilizers. In a monitored affluent, the results show the impact of the direct discharge of domestic sewage, while in the sewage treatment plant there is clear evidence of denitrification. This study demonstrated that isotope application of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- is efficient tools for identification of N-NO_3^- of synthetic fertilizers and domestic sewage.

Keywords Nitrate · Stable isotopes · Nitrate source · Fertilizers · Domestic sewage

Introduction

The watersheds used for public water supply usually do not receive adequate planning, control and management to preserve the quality of water resources. Nitrate is a common contaminant in water sources and in excess can contribute to the eutrophication of water accumulated in the reservoirs, and the intake of this water can cause diseases like methemoglobinemia and stomach cancer (Gehle 2015). In surface water used for human supply, nitrate ion concentration values should not exceed 50 mg L^{-1} to avoid harmful effects on human health (WHO 2017), and the Brazil Health Ministry Ordinance No. 2914 of 2011 indicates a concentration limit of 10 mg L^{-1} for N-NO_3^-, in drinking water.

Nitrate may originate from point or diffuse sources, such as domestic sewage and fertilizers, and may be present at various concentrations in the environment. The identification of the origin of NO_3^- in small watersheds can be accomplished by measuring the variation in ^{15}N and ^{18}O isotopes. In general, the Cartesian relation between $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- leads to typical intervals of the main sources of nitrate as well as nitrification and denitrification processes.

Several studies conducted to determine the characteristic intervals of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- were cited by Kendall et al. (2007) to demonstrate the variation range of the main sources of nitrate. The variation in the inorganic fertilizers is represented by $\delta^{15}N$-4 to + 4‰ (σ: −4 and +3‰) and $\delta^{18}O$ of +17 to +25‰, whereas organic fertilizers present greater intervals, with an amplitude of +2 to +30‰ of $\delta^{15}N$.

Microbiological action responsible for the nitrification process of fertilizer (NH_4^+) reflects a range for the $\delta^{18}O$ of −5 to +15‰. Human and animal wastes typically have a

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$\delta^{15}N$ between + 10 and + 20‰, whereas in soils without human influence, $\delta^{15}N$ can range from − 10 to + 15‰, being most often in the + 2 to + 5‰ range.

Lohse et al. (2013) evaluated the nitrification and denitrification processes by applying the methodology of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in soil, rainfall and surface water, and they related it to the terrain topographic variation. These authors observed that surface runoff and putative flow alter NO_3^- sources from subsurface water, generating an overlap of values, and that N-chemistry in streams is a complex integral of the geochemical environment of the watershed.

In agriculture, some studies of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ were also conducted to identify N-nitrate from agricultural land use. For instance, Jin et al. (2012) determined the source of groundwater nitrate in an area planted with rice in Huzhou, China. They stated that the isotopes were definitive and quite relevant in the indication that N-fertilizer, soil organic matter and manure were the dominant nitrate sources. Still in the underground environment, Minet et al. (2012) used $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ in the unsaturated zone of the soil to trace different N sources, showing that it is possible to distinguish contamination from artificial fertilizers and organic wastes. A study carried out in an agricultural area by Kelley et al. (2013) identified that in the vadose zone nitrified NH_4^+ fertilizer is the dominant source of NO_3^- in leached water and that nitrification is more effective during the low discharge season.

In watersheds with agricultural land use, the ^{15}N and ^{18}O isotopes can be employed to identify the dominant spatial, temporal and hydrological processes that affect the transported nitrate. Wexler et al. (2012) studied these processes in the Wensum watershed (Norfolk, UK) and found that $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are powerful tools in determining dominant nitrogen cycling processes and their interactions with hydrology in agriculturally impacted watersheds. This study showed that nitrate sources undergo microbially mediated nitrogen cycling and nitrification before reaching catchment waters.

In Brazil, scientific studies with isotopes of ^{15}N and ^{18}O of nitrate are scarce. Monforte (2014) tested the methodology for the analysis of isotopic variations of N (^{15}N:^{14}N) in NO_3^- from natural surface water samples collected in watersheds of the Federal District and Paranoá Lake (central region of Brazil). The results of this research demonstrated that the investigated methodology is adequate to quantify $\delta^{15}N\text{-}NO_3^-$ in natural samples with low concentrations of this ion (< 6 mg L^{-1}). There are no scientific works that deal with the application of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ to distinguish sources of nitrate in Brazil's stream waters.

The aim of this study is to show if there is any influence of the inputs used in agriculture and the derived from a wastewater treatment plant (WWTP) in the water of the tributaries of the Faxinal Dam, that provide most public water supply for the city of Caxias do Sul (Brazil), using isotopes of $\delta D\text{-}H_2O$, $\delta^{18}O\text{-}H_2O$, $\delta^{15}N\text{-}NO_3^-$, $\delta^{18}O\text{-}NO_3^-$ and $\delta^{15}N_{Fertilizer}$.

Geology and physical aspects of the studied area

The studied area is near the city of Caxias do Sul, in the State of Rio Grande do Sul, Southern Brazil. The catchment area of the Faxinal stream supplies 63% of the local urban population, representing the main source of surface water (Vargas et al. 2013). It consists of 6679 ha and is predominantly rural (Fig. 1).

The area investigated sits on the intracratonic basin of the Paraná Province, which contains the São Bento group, consisting of the sedimentary units of the Guará and Botucatu formations, and the volcanic package of the Serra Geral formation which is related to the opening of the South Atlantic Ocean. The tholeiitic volcanic package is represented by basalts to andesite-basalts in the bottom sequence and an acidic sequence of rhyolites to rhyodacites in the upper portion. These comprise two petrographic types, known as Palmas (aphyric to lightly microporphyritic) and Chapecó (porphyritic), both forming tabular layers considered as ignimbrites (Roisenberg and Viero 2000). Both the Palmas and Chapecó ignimbrites contain microphenocrysts and phenocrysts of plagioclase and clinopyroxene, submerged in the groundmass of intergrowths of micrographic quartz-feldspar, which is subvitreous in the bottom and top portions of the unit. Microlites of plagioclase, pyroxenes, amphiboles, and magnetite also appear in the groundmass.

The Caxias do Sul District region and the Faxinal watershed are mainly covered by acidic units of the Palmas type, with a total thickness of 300 m, while basalts and andesite-basalts occur in the lower levels, along the valleys, and are rarely interbedded with acidic ignimbrites (Fig. 1). In this region, there are neosols, cambisols, ultisols, oxisols, nitosols and chernosols (Streck 2008), while regolithic neosols were also identified in the area.

The Caxias do Sul district is contained within the Guaíba hydrographic region and the Taquari-Antas (G040) and Caí (G030) watersheds. The climate in the region is classified as hot temperate, with average annual temperature of 17.2 °C and average rainfall of 1915 mm per year. In addition, the months with the highest average historical rainfall are September (175 mm) and January (150 mm), while the lowest is May (50 mm), according to INMET (2014), CEMETRS (2014).

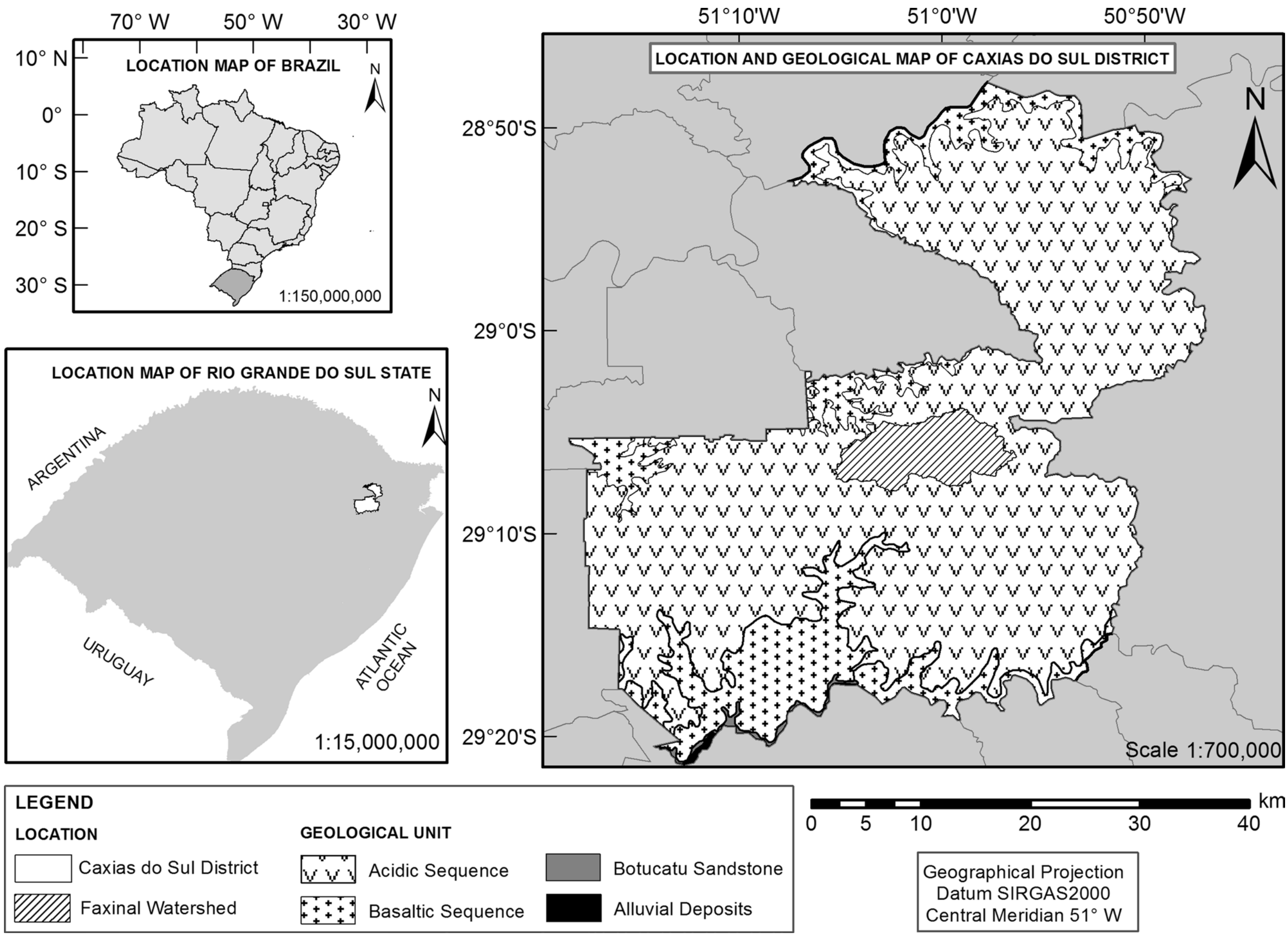

Fig. 1 Location and geological map of the Faxinal watershed and the city of Caxias do Sul. Datum SIRGAS2000, Central Meridian 51°W

Materials and methods

The land use was characterized in a geographic information system (GIS) through the analysis of satellite images, collected by GeoEye Satellite Imagery. Samples of NPK fertilizers, calcium nitrate and calcareous rock material, which are commonly used in crop cultivation, were collected directly from the farms. The catchment area of the Faxinal basin was subdivided into seven sub-basins, each one corresponding to a monitoring point (Fx-01 to Fx-07). The background and sewage treatment station points correspond to Fx-Br and Fx-ETE, respectively.

The collection points were located in tributaries in rectilinear and distant stretches of backwater area of the dam lake and in places without human influence in order to determine background concentrations (Table 1). These points correspond to the outlet of each monitored sub-basin that flows to the reservoir. The Fx-07 point is located in the tributary that receives the effluent from the sewage treatment plant, while the other points are receiving water from agricultural areas. The water aliquots were sampled on September 2, 2014.

Water samples for δ^2H-H_2O and $\delta^{18}O$-H_2O analysis were taken using polyethylene bottles, and each sample was separated into four volumes, an aliquot of 0.5 ml, two with 1 ml, and one with 1.5 ml in vials prepared with an atmosphere

Table 1 Location of sampling points and sub-basin area of each point (Datum SIRGAS2000, Central Meridian 51°W)

Point	Fx-01	Fx-02	Fx-03	Fx-04	Fx-05	Fx-06	Fx-07	Fx-Br
Lat (S)	29°5′21.7″	29°5′38.6″	29°5′43.6″	29°6′10.2″	29°6′20.5″	29°6′15.1″	29°5′54.6″	29°4′40.5″
Long (W)	51°1′20.6″	51°1′47.8″	51°2′22.4″	51°3′25.9″	51°3′47.2″	51°3′57.3″	51°4′12.4″	50°58′3.1″
Sub-basin area (ha)	2910.71	1206.90	195.65	684.09	282.87	1239.33	159.74	–

of helium and phosphoric acid. Subsequently, aliquots were sent to the Stable Isotope Laboratory at the University of Brasilia (LAIS), Brazil, and analyzed by absorption spectroscopy laser tunable diode (EALDS)-type cavity ring-down spectroscopy, with a Picarro L2120-i Analyzer. This equipment showed an associated error of 1‰ for δ^2H-H_2O and of 0.2‰ for $\delta^{18}O$-H_2O, and the international standard Vienna Standard Mean Ocean Water (VSMOW) was used. The samples of the collected fertilizer in agricultural areas were sent to LAIS for the determination of $\delta^{15}N$. The results were obtained by isotopic ratio mass spectrometry (IRMS), with a Thermo Scientific DeltaV plus IRMS equipment. The standard used was atmospheric N_2 (AIR-N).

The water sampling for the $\delta^{15}N$ and $\delta^{18}O$ analyses was performed at the end of the runoff event. Polyethylene bottles were used, and the filtration was performed under vacuum using regenerated cellulose membrane with 0.45 µm pore size. Aliquots were stored in 50-ml vials, frozen and sent to the Environmental Isotope Laboratory, University of Waterloo, Canada. The isotopic values $\delta^{15}N$ and $\delta^{18}O$ of nitrate were determined by applying the chemical denitrification method (McIlvin and Altabet 2005; Spoelstra et al. 2014). The equipment used was GVI Isoprime-IRMS (TG-IRMS). The lower limit for the analysis is 0.5 mg L^{-1} N-NO_3 (mg), samples showed little or no nitrite ($NO_2 < 2\%$ de NO_3^-), and the chloride concentration was lower than 1000 mg L^{-1}. It was necessary to quantify the concentrations of nitrate, nitrite, dissolved organic carbon (DOC) and chloride present in the samples to perform the analysis of $\delta^{15}N$ and $\delta^{18}O$. Duplicate samples and standards within each run are typically within ±0.3‰ to $\delta^{15}N$ and ±0.8‰ to $\delta^{18}O$, and the standards used for determining the $\delta^{15}N$ and $\delta^{18}O$ of nitrate in the water were AIR-N and VSMOW, respectively.

Results

The land use at the Faxinal watershed is 15% agricultural use, 0.56% construction, whereas the 84.44% is occupied by forests and pastures. The main crops identified were garlic, plums, beets, broccoli, persimmon, carrots, apples, corn, pears, radishes, cabbage, tomatoes and grapes. The largest cultivated areas occur in three sub-basins: Fx-01, Fx-02 and Fx-04. Sub-basin Fx-07 has the highest percentage of built-up area, with a wastewater treatment plant located near the urban area (represented by point Fx-ETE), in the eastern sector of the Faxinal watershed (Fig. 2).

Table 2 shows the δ values of deuterium and oxygen isotopes in water, nitrogen and oxygen isotopes in the nitrates, the ratio between $\delta^{18}O$-NO_3^- and $\delta^{15}N$-NO_3^-, the average deuterium excess, dissolved organic carbon (DOC), chloride and nitrate–N concentrations of the sampled tributaries

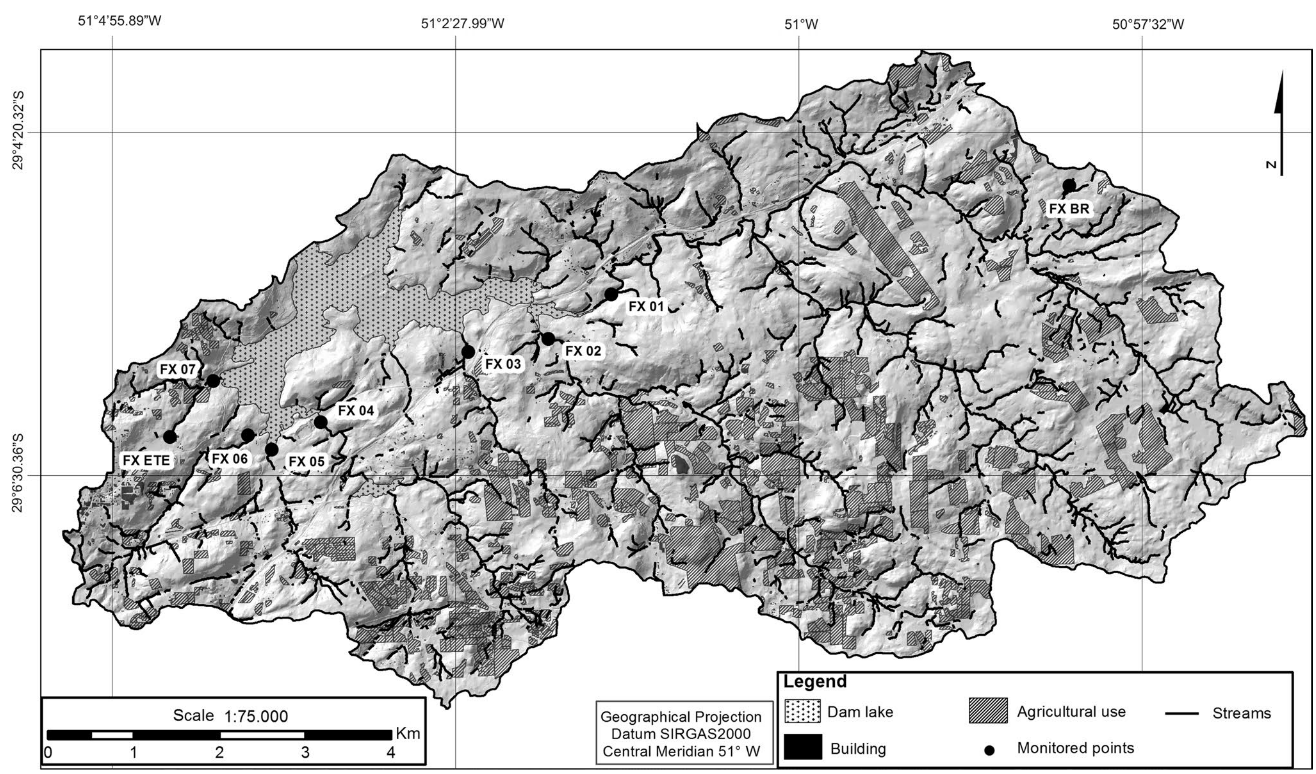

Fig. 2 Location map of the sampling points and agricultural use in the Faxinal watershed

Table 2 Comparison of δ^2H, $\delta^{18}O$, $\delta^{15}N$, $\delta^{18}O/\delta^{15}N$, N-$NO_3^-$, DOC and chloride identified in the Faxinal watershed, samples collected in the final effluent of the WWTP and of the water tributaries

Point	δ^2H-H_2O (‰)	δ^{18}O-H_2O (‰)	*d*-excess[a]	Chloride (mg L^{-1})	DOC (mg L^{-1})	N-NO_3^- (mg L^{-1})	δ^{15}N-NO_3^- (‰)	δ^{18}O-NO_3^-(‰)	$\delta^{18}O/\delta^{15}N$
Fx-01	−29.90	−5.13	11.1	3.85	4.67	0.34	7.9	8.8	1.1
Fx-02	−26.41	−4.23	7.4	4.55	7.05	0.83	7.6	9.1	1.2
Fx-03	−25.59	−4.60	11.2	4.9	9.1	0.71	9.0	10.1	1.1
Fx-04	−22.45	−3.79	7.9	4.55	6.07	0.62	8.2	9.8	1.2
Fx-05	−24.12	−4.71	13.5	4.2	8.41	0.32	3.9	21.7	5.5
Fx-06	−23.71	−4.65	13.5	4.9	7.1	0.8	5.0	19.8	3.9
Fx-07	−27.41	−2.80	−5.0	6.3	7.48	1.06	4.1	4.2	1.0
Fx-Br	−29.12	−5.07	11.4	3.5	13.81	<DL	<DL	<DL	–
Fx-ETE	–	–	–	49.7	17.03	0.51	19.4	7.2	0.4

< *DL* detection limit

[a] *d*-excess = δD–8(δ^{18}O) (Dansgaard 1964)

and the WWTP effluent. Due to the low concentration of nitrate in the background sample (Fx-Br), signal readings of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- were below the detection limit. The analyzed synthetic fertilizers (NPK and calcium nitrates) showed the following values of δ^{15}N (‰): F1 (5.6), F2 (−0.8), F3 (1.4), F4 (0.0) and F5 (−0.2).

The values of δ^2H and δ^{18}O were plotted graphically with regard to the Global Meteoric Water Line (GMWL), Local Meteoric Water Line (LMWL), Carlos Barbosa Meteoric Line and Carlos Barbosa Wells and Fountains Tendency Line. The representation of LMWL was based on data from the station located in the city of Porto Alegre (Southern Brazil) derived from Isotope Global Network Scramble International Atomic Energy Agency/IAEA (IAEA/WMO 2001). Bortolin (2014), developed the meteorological water line of Carlos Barbosa town based on the analyses of rainfall δ^2H and δ^{18}O, which varies along the year, with more positive isotope values during the months with low rainfall and more negative isotope values during high rainfall months. Carlos Barbosa town is inserted in the same climatic, geomorphological and geological context as the Faxinal watershed, 50 km far from each other. The isotopic rates analyzed in the Faxinal watershed show a distribution around the LMWL and GMWL, and between the Meteoric Line and line of tendency (wells and fountains) of Carlos Barbosa. Even though Fx-07 displaces from other controlled points, it is still within the variation range of the observed values in the wells (groundwater) and fountains (water springs), LMWL and GMWL (Fig. 3).

Dansgaard (1964) determined that the average deuterium excess (*d*) is calculated by $d = \delta D - 8(\delta^{18}O)$. Table 2 shows that the *d*-excess results are between $-5.0 \leq d \leq 13.5$‰ demonstrating that the majority of samples are similar to the local global standard for meteoric water (+10‰). In this study, the δ^2H-H_2O and δ^{18}O-H_2O values of the Carlos Barbosa town (Bortolin 2014) were used to calculate the d-excess of rainfall ($15 \leq d \leq 32.3$‰), fountains ($5.5 \leq d \leq 23.1$‰) and groundwater ($2.5 \leq d \leq 26.2$‰), which were regionalized to the area of the Faxinal watershed.

Figure 4 shows how the results of the sampled water are plotted in four different compartments (Kendall et al. 2007) in the chart of δ^{15}N-NO_3^- versus δ^{18}O-NO_3^-. The N and O isotopic compositions in the analyzed samples showed that δ^{18}O-NO_3^- values are relatively high in two streams (Fx-05 and Fx-06), while these same samples have low concentration of δ^{15}N-NO_3^-, when compared to the other results plotted in Fig. 4. On the other hand, the Fx-07 sample showed reduced concentration for both isotopes.

The signatures of δ^{15}N-NO_3^- and δ^{18}O-NO_3^- showed similar behavior in four samples (Fx-01, Fx-02, Fx-03 and Fx-04) and values less enriched in Fx-07. In other two aliquots (Fx-05 and Fx-06), there are high levels of δ^{18}O-NO_3^- and lower of δ^{15}N-NO_3^-, whereas Fx-ETE shows a much higher value of δ^{15}N-NO_3^- (Fig. 5).

Discussion

The isotopic signatures of δ^2H and δ^{18}O show a distribution around the LMWL and GMWL, and the deuterium excess is between $7.4 \leq d \leq 13.5$‰, which shows similarity with the local global standard for meteoric water (+10‰). Also, the *d*-excess is inserted in the interval $5.5 \leq d \leq 23.1$‰ (surface fountains) and $2.5 \leq d \leq 26.2$‰ (groundwater), but is lower than the rainfall values $15 \leq d \leq 32.3$‰. According to Bortolin (2014), the δ^2H and δ^{18}O values of rainfall, surface fountains and groundwater are statistically similar indicating that rainfall recharges the shallow aquifers. Fx-07 presented discrepant d-excess in relation to the other observed values (−5.0‰), which suggests that there is a contribution

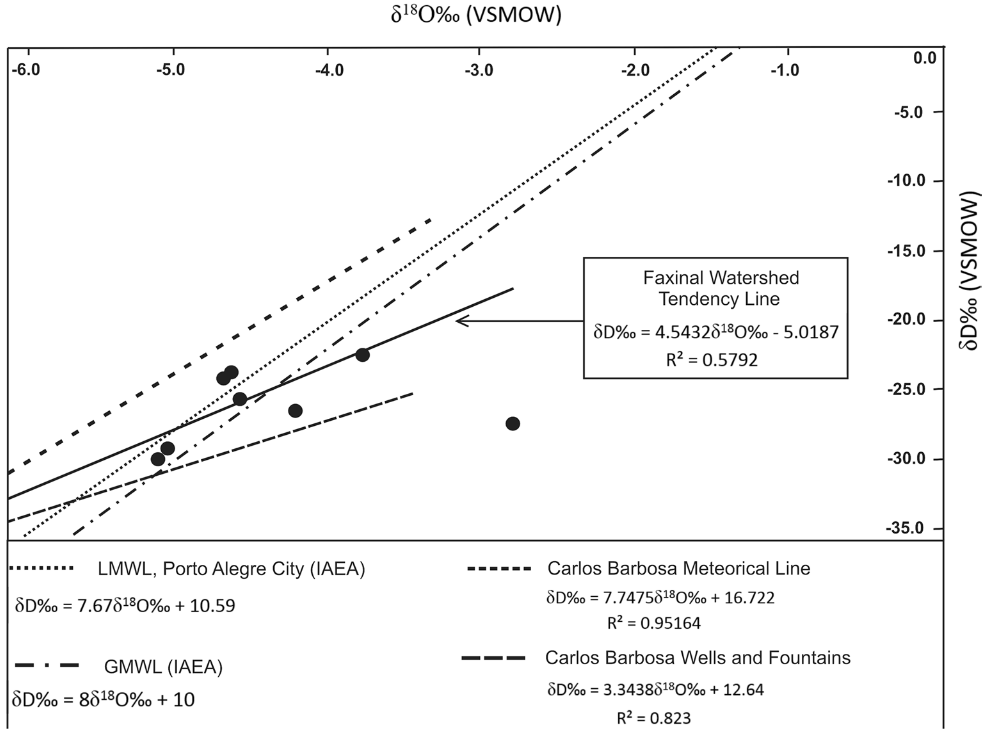

Fig. 3 Comparative values of δ2H-H_2O and δ^{18}O-H_2O identified in the study area samples with GMWL, LMWL, Carlos Barbosa Meteoric Line and Carlos Barbosa Wells and Fountains Tendency Line

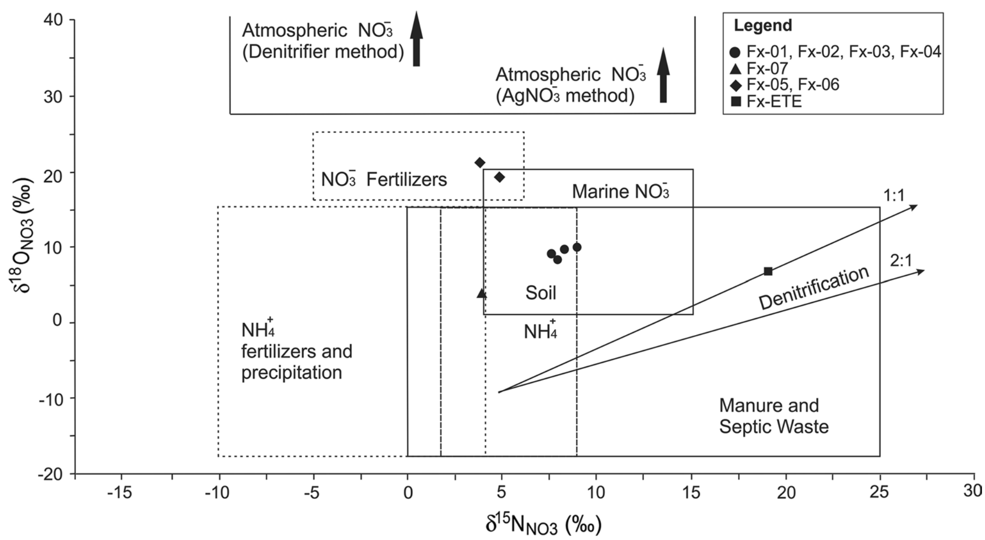

Fig. 4 Settling of the values of the isotopic rates analyzed in this study, plotted on the graph of typical δ^{15}N-nitrate and δ^{18}O-nitrate values derived from various sources of nitrogen. Extracted and modified from Kendall et al. (2007)

of groundwater through ascending supplies. In addition, δ^{18}O value equal to −2.8‰ was observed, demonstrating a heavier isotopic composition. According to Wood (2001), isotopically heavy water in δ^{18}O shows a negative *d*-excess, reflecting evaporation of recharge water before infiltration. The evaporation process that occurs under unbalanced and fast conditions can result in excess negative deuterium in water (Dansgaard 1964).

The δ^{15}N-NO_3^- values observed in the samples are situated between 3.9 and 19.4‰, whereas in the fertilizer δ^{15}N ranged from −0.8 to 5.6‰. In the fertilizer (F1), the δ^{15}N value is superimposed with the values of some tributaries of the catchment, which have the lightest isotopic composition (Fx-05 and Fx-06). The δ^{18}O-NO_3^- isotope is the key determinant for the identification of nitrate sources, especially when the δ^{15}N values are not discriminating.

Atmospheric and fertilizers nitrate sources have a δ^{18}O-NO_3^- isotopic composition considerably larger than δ^{15}N-NO_3^-, resulting in a ratio > 1, as demonstrated by Wexler et al. (2012). In this study, the ratio δ^{18}O-NO_3^-/δ^{15}N-NO_3^- is well above this threshold in the samples Fx-05 (5.5) and Fx-06 (3.9), allowing to clearly

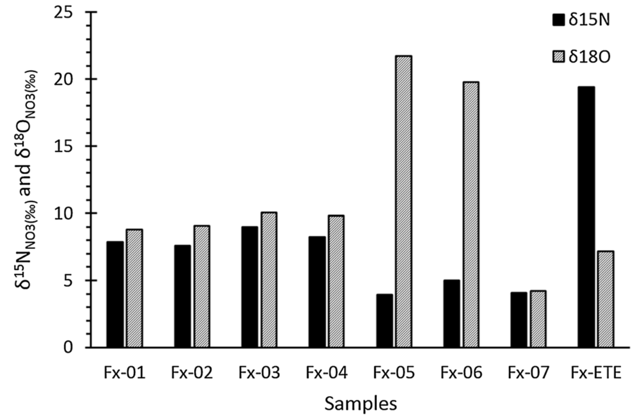

Fig. 5 Behavior of $\delta^{15}N$-NO_3^- and $\delta^{18}O$-NO_3^- values identified in the analyzed samples in the Faxinal watershed

identify the synthetic fertilizer contribution (Fig. 3), while Fx-01 through Fx-04 have values close to 1 (Table 2). This relationship is even more striking in the case of Fx-ETE, where it reaches 0.4, and in the case of Fx-07 point, which is influenced by the WWTP effluent and coincides with the limit (1.0).

The relationship between nitrate concentration (mg L^{-1}) with $\delta^{15}N$ and $\delta^{18}O$ can be decisive in the interpretation of nitrification and denitrification processes in small watersheds. An increase in the concentration of NO_3^- and a decrease in $\delta^{15}N$ suggest the influence of nitrification processes, whereas the reverse situation is interpreted as resulting from the denitrification (Cummings 2015). In the studied tributaries, a relative dispersion of N-NO_3^- (mg L^{-1}) values relative to $\delta^{15}N$ and to $\delta^{18}O$ was identified, which may be the result of the behavior of the ground biomass (Fig. 6). This lack of correlation has been emphasized in other regions by BryantMason et al. (2012), who studied the Mississippi and Atchafalaya (USA) Rivers systems and Chang et al. (2002) in the Mississippi River Basin.

In a study on the effect of land use in agricultural river systems of Germany, Deutsch et al. (2006) found that 86% of the nitrate present in river water originated from agricultural drainage water. Kendall et al. (2007) reported that isotopic signatures linked to artificially fertilized agricultural soils can be related to the increased $\delta^{15}N$ originating from the denitrification process. These authors also stated that poorly drained fine-grained soils contribute to the development of the denitrification process.

The denitrification process provides, progressively, nitrate with heavier isotopes due to the fractionation of nitrogen and oxygen and occurs simultaneously with the reduction in concentration of nitrate (Kendall et al. 2007). The fractionation $\delta^{15}N$-NO_3^- can increase during the microbiological assimilation stage, generating an elevation of $\delta^{15}N$ values (Wexler et al. 2012). In this study, the Fx-ETE sample,

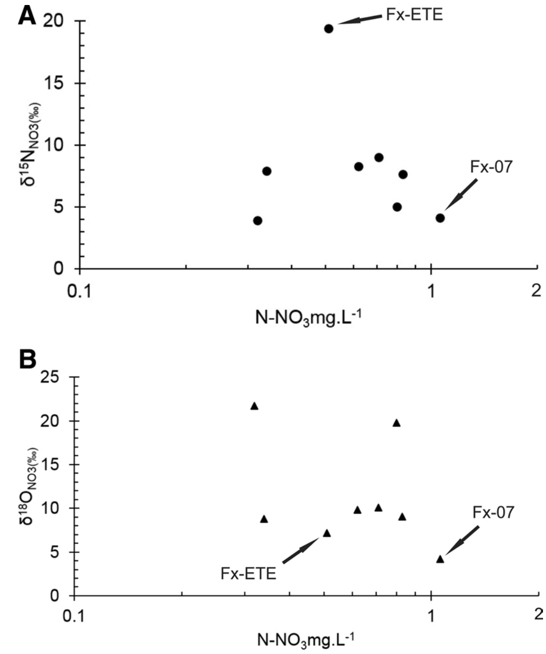

Fig. 6 $\delta^{15}N$-NO_3^- versus N-NO_3^- (mg L^{-1}) plot in chart 6A and $\delta^{18}O$-NO_3^- versus N-NO_3^- (mg L^{-1}) plot in chart 6B, for samples collected in the final effluent of the WWTP and in the tributaries of the Faxinal watershed

which represents the final effluent from the treatment process in the WWTP, showed relatively low concentrations of N-NO_3^- (mg L^{-1}), high chloride contents (mg L^{-1}) and high values of $\delta^{15}N$-NO_3^- (Table 2), evidencing the denitrification process. The fractionation of nitrogen and oxygen most likely happened in the sewage treatment plant during the Taboa (*Typha latifolia*) nitrogen fixation in the constructed wetlands.

At the Fx-07 sampling point, which corresponds to the downstream of the WWTP, the concentration of chloride is enriched in relation to the other tributaries of the catchment area, the concentration of N-NO_3^- is the highest in the sample group, and the $\delta^{15}N$ isotopic composition shows a signature compatible with septic wastes. Besides the influence of the WWTP effluent, the tributary may be receiving sewage intake without treatment from residences without connection to the sewage network, which explains the higher concentration of N-NO_3^-, while $\delta^{15}N$-NO_3^- values are not as expressive.

Conclusion

Isotopic analyses of N and O were performed on the waters of the Faxinal Dam watershed, near the city of Caxias do Sul, Southern Brazil, to determine the influence of agriculture and the effluent from the sewage treatment plant on the water, which is the main source of domestic water supply to the local population. δ^2H and $\delta^{18}O$ isotopic compositions demonstrate that the deuterium excess in the background sample (Fx-Br) and in six of the seven analyzed streams (Fx-01 to Fx-06) is statistically similar to the waters represented by the trend line (wells and sources) of Carlos Barbosa and LMWL for meteoric water (+ 10‰). However, one of the streams (Fx-07) already shows a possible influence of groundwater in its composition. The values of $\delta^{15}N\text{-}NO_3^-$ in the tributaries are markedly lower than those found in the effluent treatment plant (Fx-ETE), which has low concentrations of $N\text{-}NO_3^-$ and high chloride levels. On the other hand, the enrichment of chloride and $N\text{-}NO_3^-$ registered at the sample point located downstream (Fx-07) of the WWTP, compared to the water of other tributaries, suggests contamination from septic wastes, as shown by the isotopic signature of $\delta^{15}N\text{-}NO_3^-$. In the other sampling points, corresponding to other tributaries, the $\delta^{18}O\text{-}NO_3^-/\delta^{15}N\text{-}NO_3^-$ ratio demonstrates the influence and contribution of synthetic fertilizers.

This study demonstrated that isotope application of $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ is efficient tools for the identification of $N\text{-}NO_3^-$ of synthetic fertilizers and domestic sewage. The use of this technique and methodology in waters of watersheds used for drinking water supply is unprecedented in Brazil, so it can be used as a reference for geochemical studies based on the watershed management. As future improvement in this research, it would be interesting to increase the amount of analyzed samples and distribute them throughout the seasons to perform a statistical evaluation of the isotopic values and also to understand the seasonality of the contaminating sources.

Acknowledgements The authors thank the Municipal Autonomous Service of Water and Sewage of the city of Caxias do Sul for the great support for this research.

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