# NITRATE IN GROUNDWATER IN RIBEIRÃO PRETO CITY AREA IN BRAZIL

ANTONIO LUIZ CERDEIRA*
LOURIVAL COSTA PARAIBA**
KAREN KATAGUIRI***
DENIZART BOLONHEZI****
MARCO ANTONIO FERREIRA GOMES*****
CLAUDIO APARECIDO SPADOTTO**
CARLOS FARJANI NETO******
MARCUS BARIFOUSE MATALLO*******
HENRIQUE MOMM********

The region of Ribeirão Preto City, southeastern Brazil, is an important sugar cane and recharge area for groundwater of the Guarany aquifer. This research was conducted to evaluate the potential contamination of groundwater with nitrates in the area and in surrounding municipal wells. No significant amount of nitrate was found in the recharge agricultural area. However, nitrate levels were detected at concentrations higher than the Maximum Concentration Level (MCL) of 6.0 mg/L in a downtown, urban, well located away from agriculture, which had no history of nitrogen application, reaching values higher than the maximum risk coefficient for infants (RC) of 1.0.

*KEY-WORDS: GROUNDWATER; NITRATE; SUGARCANE; RISK CONTAMINATION INDEX.*

* Pesquisador, Ph.D. em Fisiologia Vegetal, Embrapa Meio Ambiente, Jaguariúna, SP, Brasil (e-mail: cerdeira@cnpma.embrapa.br).
** Pesquisador, Ph.D. em Matemática, Embrapa Meio Ambiente, Jaguariúna, SP, (e-mail: lourival@cnpma.embrapa.br; spadotto@cnpma.embrapa.br).
*** Estudante, Embrapa Meio Ambiente, Jaguariúna, SP, Brasil.
**** Pesquisador, Ph.D. em Agronomia, Instituto Agronômico de Campinas, Ribeirão Preto, SP, Brasil (e-mail: denizart@apta.sp.gov.br).
***** Pesquisador, Ph.D. em Geologia, Embrapa Meio Ambiente, Jaguariúna, SP, Brasil (e-mail: gomes@cnpma.embrapa.br).
****** Químico, Departamento de Água e Esgoto de Ribeirão Preto, Ribeirão Preto, SP, Brasil (e-mail: laboratorio@daerp.pmrp.com.br).
******* Pesquisador, Doutor em Edafologia Y Química Agrícola, Instituto Biológico de Campinas, Campinas, SP, Brasil (e-mail: matallo@biologico.sp.gov.br).
******** Professor, Ph.D. in Geologia, Department of Geology and Geological Engineering, The University of Mississippi, University, MS, United States (e-mail: hmomm@olemiss.edu).

## 1 INTRODUCTION

The region of Ribeirão Preto city, São Paulo State, located southeast of Brazil, is an important area for sugar cane production, with high levels of herbicide and fertilizer utilization. It is also an important recharge area for the Guarany aquifer ground water, which extends to eight Brazilian states and part of Argentina, Uruguay, and Paraguay, with approximately 1,200,000 $km^2$. Geological studies in the region have identified a watershed, called Espraiado, with a high risk of groundwater contamination. Certain areas of the watershed are composed of highly permeable sandy soil which allows leaching of agrochemicals applied to crops (MIKLOS & GOMES, 1996).

Several studies conducted in the region have detected low levels of applied pesticides in the groundwater on sugar cane areas (LANCHOTE et al., 2000; CERDEIRA et al., 2000; GOMES, SPADOTTO & LANCHOTE, 2000). One of those studies ranked counties by contamination risk levels, defining priority regions for monitoring programs for nitrates (RODRIGUES, PARAÍBA & BUSCHINELLI, 1997). Due to the high permeability of some soils present in this region, the high mobility of the herbicides and fertilizers applied, and being a recharge area, it is important to investigate the potential transport of fertilizers to underlying aquifers. The cultivation of sugar cane in this area demands the frequent use of nitrogen as a fertilizer. Nitrogen is applied as granules at planting at rate of 30 kg/ha. After each harvest, each year, it is applied at a rate of 60 to 120 kg/ha. Variable amounts of herbicides such as diuron, hexazinone, 2,4-D, ametryn, and tebuthiuron are used. Besides nitrogen, fertilizers based on phosphorus and potassium at rate of 160 and 180 kg/ha, respectively, are also applied. Studies have shown that nitrate groundwater contamination can be a problem due to the massive use of fertilizers in agriculture (RODRIGUES, PARAÍBA & BUSCHINELLI, 1997), especially in this vulnerable recharge area of the Guarany aquifer in the region.

Drinking water and dietary sources of nitrate and nitrite can react with amines and amides to form potent animal carcinogens from *N*-nitroso compounds. Nitrate is also widespread contaminant of drinking water, especially in agricultural areas (WARD et al., 2007; DE JONG et al, 2007). The health effects of contamination are due to the transformation of nitrates into nitrites and possibly the transformation of nitrites into nitrosamines in the stomach. High levels of nitrate can also cause methemoglobinemia in infants, deformation of hemoglobin, due to its presence in water used to reconstitute milk for feeding (LEVALLOIS & PHANEUF, 1994; ALABURDA & NISHIMURA, 1988; SACCO et al., 2007). Affected infants develop a peculiar blue-gray skin color and may become irritable or lethargic, depending on the severity of their condition (KNOBELOCH et al., 2000). According to a São Paulo State law in Brazil, the maximum concentration level (MCL) of nitrates in water is 6.0 mg/L (ALABURDA & NISHIHARA, 1998). Due to the watershed vulnerability and high impute of nitrogen fertilizer applied, this research was conducted to characterize the potential contamination of groundwater with nitrates in the recharge area of groundwater and its vicinity.

## 2 MATERIALS AND METHODS

A survey conducted in the area has indicated that nitrogen fertilizer was regularly utilized and it was therefore chosen for this study. Seven groundwater sample locations were selected in the recharge area watershed, during the years of 2005 and 2006. Samples were collected from wells during the months of March, July, and December of each year (Figure 1).

Groundwater was also collected during the same months from five county municipal wells located outside the watershed at the vicinity of the recharge area in addition to a well located in downtown, far away from any agricultural activities (Figure 1). The following six urban wells were studied: Central, Palmares, Portinari, Recreio Internacional, São Sebastião, and São José. Three replications were collected at each site (Table 1). Those wells were selected based on risk contamination of groundwater which is higher in the agricultural area since it is a recharge region. Samples were also collected during several months to evaluate the effect of rain on nitrate leaching.

**FIGURE 1 - LOCATION OF THE WELLS IN RIBEIRÃO PRETO COUNTY AND VICINITY WHERE THE STUDY WAS CONDUCTED IN SÃO PAULO STATE IN BRAZIL**

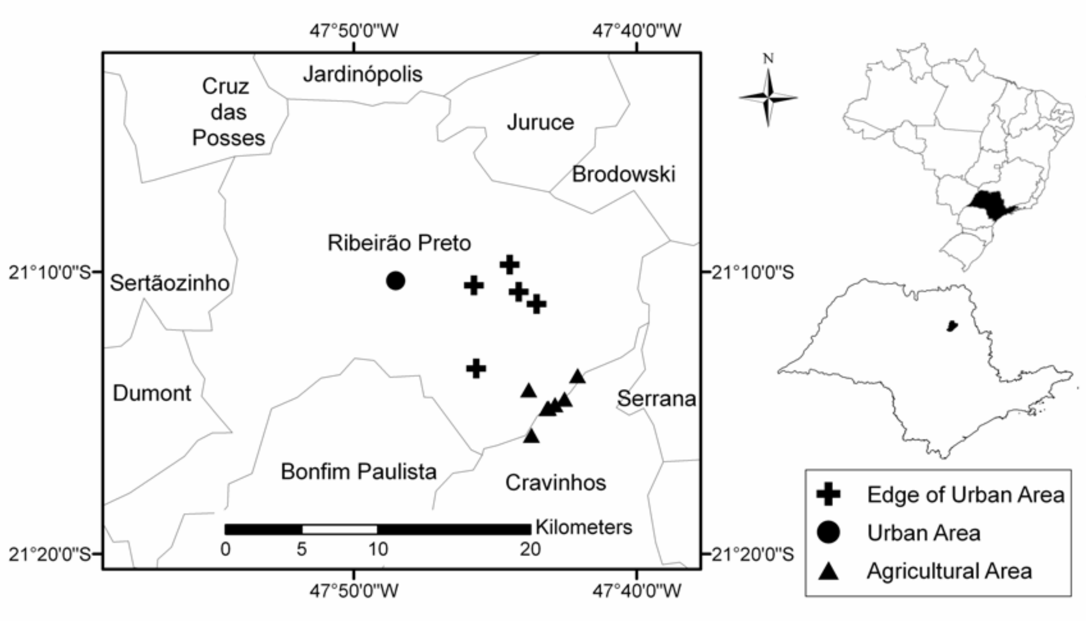



**TABLE 1 - DEPTHS AND LOCALIZATION OF THE WELLS**

| Wells | Depths (m) | Localization (South and West) |
|---|---|---|
| São Sebastião[a] | 197 | 21° 10' 43" and 47° 44' 10" |
| Palmares[a] | 199 | 21° 10' 29" and 47° 45' 45" |
| São José[a] | 236 | 21° 13' 25" and 47° 45' 40" |
| Recreio Internacional[a] | 134 | 21° 11' 09" and 47° 43' 32" |
| Central[a] | 79 | 21° 10' 19" and 47° 48' 31" |
| Portinari[a] | 220 | 21° 09' 45" and 47° 44' 29" |
| W1[b] | 53 | 21º 13' 40" and 47º 42' 05" |
| W2[b] | 38 | 21º 14' 30" and 47º 42' 33" |
| W3[b] | 8 | 21º 14' 49" and 47º 43' 07" |
| W4[b] | 4 | 21º 14' 50" and 47º 43' 10" |
| W5[b] | 9 | 21º 14' 42" and 47º 42' 53" |
| W6[b] | surface | 21º 15' 47" and 47º 43' 43" |
| W7[b] | 9 | 21º 14' 10" and 47º 43' 49" |

[a]Denotes municipal wells.[b]Denotes wells on the recharge area, from 1 to 7.

Soil samples from the sugarcane watershed were characterized by the determination of the sand, clay and silt content and granulometry. The sampled soils were classified as Typic Haplorthox, Typic Eutrorthox, Quartzipsammentic Haplorthox, and Typic Quartzipsamment. They were submitted to leaching studies in the laboratory with samples from the watershed. The data have shown the clayey Typic Haplorthox, Typic Eutrorthox, and sandy loam Quartzipsammentic Haplorthox soils had medium infiltration potential of water as opposed to Typic Quartzipsamment that showed a high infiltration potential (MIKLOS & GOMES, 1996). The main properties of some of those soils were measured by SPADOTTO, GOMES & HORNSBY (2002) and are shown on Tables 2, 3, and 4.

**TABLE 2 - QUARTZIPSAMMENTIC HAPLORTHOX SOIL PROPERTIES**

| Depth (cm) | Clay Content (%) | Porosity (%) | (%)Field Capacity | Bulk Density ($g/cm^3$) | Organic Carbon (%) |
|---|---|---|---|---|---|
| 0 – 20 | 24 | 55.8 | 22.3 | 1.29 | 0.72 |
| 20 – 40 | 26 | 62.1 | 21.7 | 1.22 | 0.50 |
| 40 – 60 | 30 | 54.9 | 21.3 | 1.21 | 0.34 |
| 60 – 80 | 29 | 54.4 | 20.2 | 1.28 | 0.25 |
| 80 – 100 | 32 | 56.5 | 19.6 | 1.21 | 0.22 |
| 100 – 120 | 34 | 51.7 | 18.8 | 1.16 | 0.20 |

**TABLE 3 - TYPIC HAPLORTHOX SOIL PROPERTIES**

| Depth (cm) | Clay Content (%) | Porosity (%) | (%)Field Capacity | Bulk Density ($g/cm^3$) | Organic Carbon (%) |
|---|---|---|---|---|---|
| 0 – 20 | 68 | 58.2 | 26.2 | 1.37 | 1.38 |
| 20 – 40 | 74 | 57.7 | 24.6 | 1.38 | 1.05 |
| 40 – 60 | 73 | 60.4 | 23.5 | 1.32 | 0.87 |
| 60 – 80 | 70 | 61.6 | 23.1 | 1.19 | 0.67 |
| 80 – 100 | 67 | 65.2 | 22.8 | 1.16 | 0.64 |
| 100 – 120 | 63 | 64.7 | 21.4 | 1.18 | 0.60 |

**TABLE 4 - TYPIC QUARTZIPSAMMENT SOIL PROPERTIES**

| Depth (cm) | Clay Content (%) | Porosity (%) | (%)Field Capacity | Bulk Density ($g/cm^3$) | Organic Carbon (%) |
|---|---|---|---|---|---|
| 0 – 20 | 6 | 44.6 | 19.4 | 1.46 | 0.30 |
| 20 – 40 | 8 | 62.5 | 18.7 | 1.52 | 0.24 |
| 40 – 60 | 11 | 61.0 | 17.3 | 1.48 | 0.20 |
| 60 – 80 | 8 | 42.3 | 17.0 | 1.46 | 0.13 |
| 80 – 100 | 7 | 57.6 | 16.5 | 1.45 | 0.08 |
| 100 – 120 | 10 | 61.7 | 16.1 | 1.44 | 0.03 |

Water samples (1 L) were collected and nitrate was analyzed by the Cadmium Reduction Method according to GREENBERG, CLESCERI & EATON (1992), with limit of detection of 0.01 mg/L. Health risks for the population were estimated according to ARUMI et al. (2006), combining the following factors expressed as Risk Coefficient (*RC*):

$$RC = \frac{\left[\dfrac{C \times V \times EF}{BW \times 365}\right]}{RfD}$$

where:

*R* = was a function of *C*, the nitrate concentrations (mg/L) found in each well (Tables 5 and 6);
*V* = volume of water ingested in L/Day (2.0 for adults and 0.64 for infants);
*EF* = exposition frequency in days/year (350);
*BW* = body weight (70 and 4.0 kg for adults and infants, respectively);
*RfD* = reference concentration, which is the safe maximum level of exposition that causes no harm.

This was obtained from literature from toxicological studies (USEPA, 2008). In this case, the *RfD* was 1.6 mg $kg^{-1}$ $day^{-1}$. *RC* can vary from zero, no-risk, to 1.0 or more, highest risk.

## 3 RESULTS AND DISCUSSION

Very low amounts of nitrate residues were detected in groundwater of the recharge, agricultural area, where fertilizer (nitrogen) is applied (Table 5), even though a non-confined superficial water table with depths varying between zero to 20 m (Table 1). This area is also made of porous and sandy soil (MIKLOS & GOMES, 1996). Analyses of municipal wells located at the edge of the recharge area have also shown low levels of nitrate (Table 6). However, nitrate levels were detected at concentrations higher than the MCL of 6.0 mg/L in downtown, urban, and central well located away from agricultural sites with no history of fertilizer or nitrogen application (Table 6).

**TABLE 5 - AVERAGE VALUES OF NITRATE $NO^-_3$ (mg/L) DURING THE MONTHS OF MARCH (MARC), JULY, AND DECEMBER (DECE) OF YEARS OF 2005 AND 2006 IN GROUNDWATER FROM WELLS LOCATED IN THE RECHARGE AREA, SUGARCANE FIELDS**

| Wells | 2005 | | | 2006 | | |
|---|---|---|---|---|---|---|
| | Marc | July | Dece | Marc | July | Dece |
| W1 | 0.50 | 0.33 | 0.47 | 0.47 | 0.33 | 0.40 |
| W2 | 0.50 | 0.33 | 0.37 | 0.43 | 0.50 | 0.27 |
| W3 | 0.17 | 0.03 | 0.33 | 0.33 | 0.27 | 0.43 |
| W4 | 0.50 | 0.53 | 0.47 | 0.17 | 0.27 | 0.33 |
| W5 | 0.43 | 0.43 | 0.30 | 0.27 | 0.37 | 0.37 |
| W6 | 0.67 | 0.47 | 0.53 | 0.47 | 0.43 | 0.43 |
| W7 | 0.50 | 0.50 | 0.17 | 0.37 | 0.47 | 0.37 |

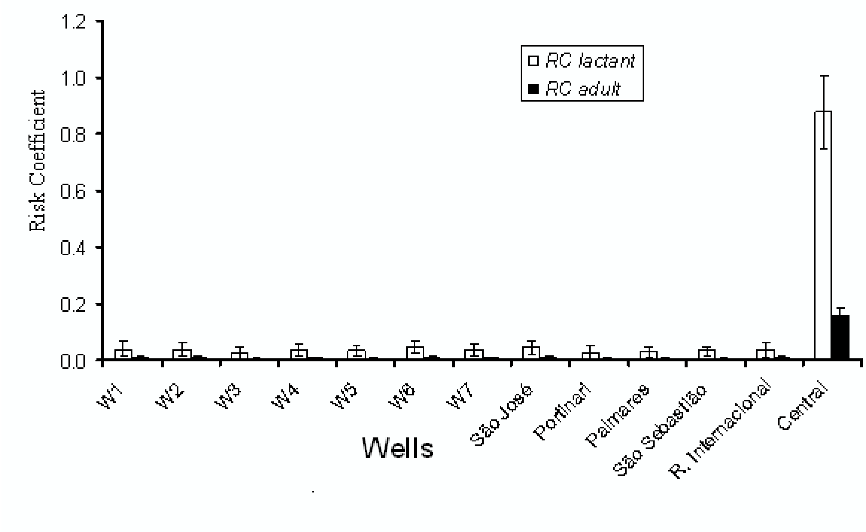
**TABLE 6 - AVERAGE VALUES OF NITRATE $NO^-_3$ (mg/L) DURING THE MONTHS OF MARCH (MARC), JULY, AND DECEMBER (DECE) OF YEARS OF 2005 AND 2006 IN GROUNDWATER FROM WELLS LOCATED INSIDE URBAN AREA**

| Wells | 2005 | | | 2006 | | |
|---|---|---|---|---|---|---|
| | Marc | July | Dece | Marc | July | Dece |
| São José | 0.60 | 0.47 | 0.50 | 0.47 | 0.43 | 0.37 |
| Portinari | 0.13 | 0.07 | 0.13 | 0.30 | 0.53 | 0.40 |
| Palmares | 0.30 | 0.17 | 0.37 | 0.20 | 0.47 | 0.27 |
| São Sebastião | 0.37 | 0.40 | 0.33 | 0.23 | 0.30 | 0.40 |
| R. Internacional[a] | 0.23 | 0.30 | 0.50 | 0.30 | 0.40 | 0.53 |
| Central[b] | 9.60 | 7.43 | 9.20 | 10.17 | 9.67 | 8.87 |

[a]Recreio Internacional. [b]Well located in downtown away from the recharge area.

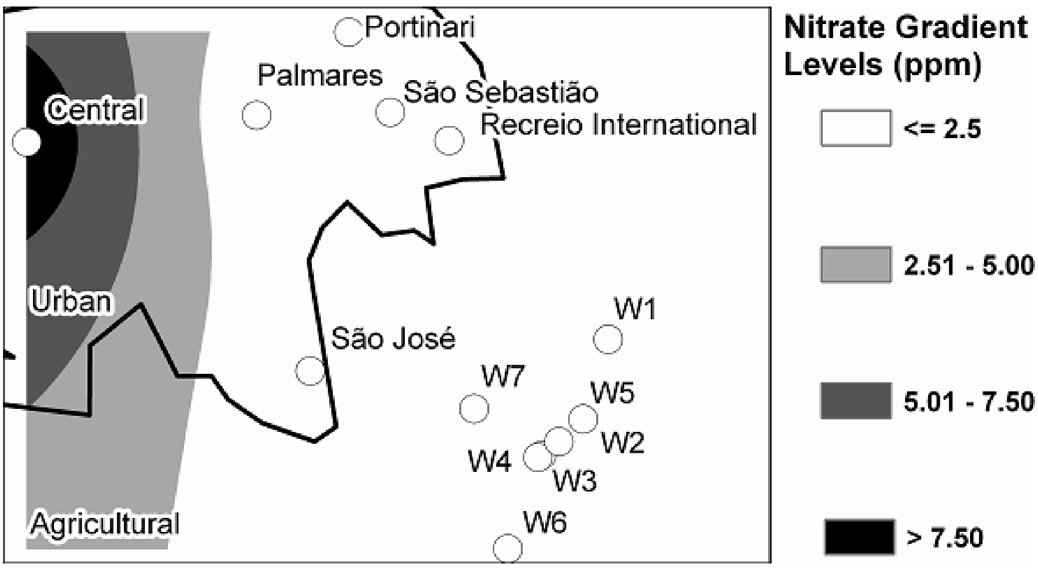
*RC* Index evaluation has also shown values close to zero for all the wells with the exception of that in the central region, located in an urban, non agricultural area. In this central area well was found an *RC* index of nitrate around 1.0, a health hazard, particularly for infants (Figure 2)**.** This was also found in an aquifer beneath the old industrial city of Nottingham, UK, in shallow ground water originated mainly from residential and industrial areas, where high nitrate concentrations probably arising from leaking sewers and contaminated land were detected (TROWSDALE & LERNER, 2007). ARUMI et al. (2006) also found in the Parral region of Chile, nitrate contamination of wells primarily linked to certain factors such as construction practices and the proximity of livestock. There was no risk found for the adult population, but there was for infants fed on formula mixed with water coming from the contaminated wells. ALABURDA and NISHIMURA (1998) also found high levels of nitrate in the metropolitan area of São Paulo city in Brazil.

**FIGURE 2 - RC (RISK COEFFICIENT) VALUES FOR SELECTED WELLS. W DENOTES RECHARGE AREA WELLS**




The data obtained were plotted using a gradient evaluation comparing areas and the results are shown on a grid of the concentrations. The samples were interpolated into a grid with 25 meters cells using the Ordinary Kriking method (OLIVER, 1990; ROYLE, CLAUSEN & FREDERIKSEN, 1981), suggesting a correlation between urban areas and the high nitrate concentration (Figure 3).

**FIGURE 3 - NITRATE GRADIENT LEVELS GRADIENT DETECTED IN THE WELLS LOCATED IN AGRICULTURAL (W) AND URBAN AREA**




Other studies have also concluded that the principal cause of groundwater contamination by nitrate are the urban and industrial wastes dumped in the environment without treatment, and that contamination by agriculturally related fertilizers is a secondary cause (SCHALSCHA et al., 1979). According to studies conducted by ARUMI, OYARZUN & SANDOVAL (2005) contrary to expectations, the aquifers of the Central Valley of Chile also appear free from any significant nitrate pollution from agricultural sources in spite of the high levels of nitrogen-based fertilizers used in the agricultural activity, the irrigation practices and the active surface water-groundwater interactions. The industrial and sewage effect on nitrate contamination were common in Chile, England and Brazil.

ARUMI, OYARZUN & SANDOVAL (2005) also afirmed that this could be due to a possible dilution effect that the amount of groundwater has on chemicals entering the groundwater system or related to the anion exchange capacity, which is also very high in studied area. Another reason pointed out by the author could be due to a denitrification process by the presence of biodegradable organic carbon and the presence of denitrifying bacteria, which are usually found in natural systems. The existence of naturally high levels of organic carbon in the soils of the present study would contribute to this. Also, according to ARONSSON and BERGSTRÖM (2001), the presence of a cover crop, such as sugar cane in this study, has a significant effect on decreasing nitrate leaching. KRAMER et al. (2006) also found a filter effect of soil organic matter on nitrate leaching. This information is important for the environmental safety of sugarcane and ethanol industry in Brazil.

## 4 CONCLUSION

Results from this study have shown that nitrate was detected at levels higher than the MCL of 6.0 mg/L in wells located in downtown areas, which are away from the sugarcane plantations. Risk analysis has shown that the dangerous level in wells located in downtown is a health hazard mainly for infants, reaching high risk levels (*RC*) of 1.0. This information is important for the ethanol and sugarcane industries since it is shown that, at least in terms of nitrate contamination, is safer than sewage and industrial activities.


## RESUMO

### NITRATOS EM ÁGUAS SUBTERRÂNEAS NA REGIÃO DA CIDADE DE RIBEIRÃO PRETO, SÃO PAULO, BRASIL

A região da cidade de Ribeirão Preto, sudeste do Brasil, é uma importante área de cultivo de cana-de-açúcar e de recarga de águas subterrâneas do aquífero Guarani. Esta pesquisa foi realizada para avaliar o potencial de contaminação de águas subterrâneas com nitrato na área e nos poços de municípios vizinhos. Não foi encontrada quantidade significativa de nitrato nas áreas de recarga e agricultura. Entretanto, níveis de nitrato foram detectados em concentração máxima de 6,0 mg/L em poço localizado no centro urbano longe de áreas plantadas, sem histórico de aplicação de nitrogênio, alcançando valores mais altos que o coeficiente de risco maximo para crianças (CR) de 1.0.



*PALAVRAS-CHAVE: ÁGUAS SUBTERRÂNEAS; NITRATO; CANA-DE-AÇÚCAR; POTENCIAL DE CONTAMINAÇÃO.*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